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A CONTRIBUTION TO RESEARCH ON NICKEL HYDROXIDES

Jean Labat

N72-32157

(NASA-TT-F-14448) A CONTRIBUTION TO RESEARCH ON NICKEL HYDROXIDES J. Labat (NASA) Jun. 1972 69 p CSCL 07D Unclas G3/06 43711

Translation of "Contribution a l'etude des hydroxydes de nickel", Annales de Chimie, Vol. 9, No. 7-8, July and August, 1964, pp. 399-427.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 JUNE 1972

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Labat, Jean. "Contribution a l'etude des hydroxydes de nickel". Annales de Chimie. Vol. 9 No. 7-8, 399-427 (juillet-Aout, 1964).

A CONTRIBUTION TO RESEARCH ON NICKEL HYDROXIDES

by Jean Labat*

Introduction

We have demonstrated in a preceding article (Ref.1) the extent of difference in opinion of various authors on the nature and the very existence of oxides and hydroxides of nickel with valences greater then two; despite a considerable amount of research on their composition and structure, no systematic research has yet been conducted on their magnetic properties. We shall mention only the work of Miss Veil (Ref. 2) on their evolution -- when immersed in water -- of the nickel hydroxide and of the hydrate of nickel sesquioxide, the results obtained by Bhatangar and Bal (Ref.3) which agree on the existence of the definite NiO oxide and, finally, the recent short thermomagnetic study of $Ni_2O_3H_2O$ made by Richardson (Ref. 4).

Without any doubt, this investigation method should be particularly interesting as the oxidation degree directly related to the valence of the nickel in these compounds must evidently

* A doctorate thesis in physics, Bordeaux, 1964.

affect their magnetic characteristics; For this reason we have undertaken a study of magnetism in these oxides, their chemical analysis, the X-ray spectrum and their electrochemical properties depending upon the method used in their preparation.

PART I

Crystallographic and magneto-chemical study of nickel hydroxides obtained by the wet method.

PREPARATION

The studied components have been prepared using precipitation and simultaneous oxidation of $Ni(OH)_2$ by various oxidizing agents (persulfate, hypochlorite and hypobromite of sodium); In order to avoid carbonation, these preparations are made in a vacuum: the installation consists, essentially, of an erlenmeyer flask with a 1500 cu cm capacity topped with a dropping bromine funnel of 500 cu cm equipped with a mercury valve. These parts are supported by a magnetic agitator. The air tightness is achieved by means of conic lapping devices.

Solution A is introduced into the erlenmeyer and strongly agitated, whereupon solution B is added drop by drop by means of a bromine dropping funnel (Table I). The inversions effected in the composition of these two solutions are for the purpose of determining the effect of the preparation method upon the nature of the compounds obtained. The precipitate is then left to rest one whole day, washed with iced water many times, until the alkalinity

disappears completely, first through decantation, later by centrifugation, it is drained and finally dried in a vacuum in $CaCl_2$. The chemical products utilized are of the R.P. quality, of the Prolabo origin.

Analysis

We have successively determined the content of active oxygen, nickel and water in different samples. The dosage of active oxygen has been effected by classical iodometry: the precipitate is dissolved in SO_4H_2 (0,1 N) in the presence of KI and the freed iodine is proportioned by a titrated solution of thiosulfate of sodium; the proportion of nickel is effected by electrolysis (Ref.5) in the form of nickel sulfate in an ammoniacal medium by means of a Prolabo unit with a revolving electrode. The water content has been mainly determined by the difference -- after controlling and determining that this value is in good agreement with the amount of freed water vapor -- by calcination at 1000° in a flux of dry nitrogen and absorbed by $CaCl_2$.

The results obtained are assembled in Table II, in which we present the elementary formula of compounds reduced to one nickel atom. This method of recording facilitates the display of their oxidation and hydration level. However, it should be pointed out that it is effectively a consideration of hydroxides as proven by X-ray spectra and not of hydrated oxides.

The diffractograms have been recorded by means of a Philips diffractometer using the K_α radiation of copper at 40kv - 20 mA

Table I. Preparation of superior hydroxides of nickel by the wet (humid) method.

Samples	Solution A	Solution B
1*a* à 9*a*	$Ni(NO_3)_2, 6\,H_2O$ = 100 g water = 500 cm³ $S_2O_3Na_2$ = 0 ; 8 ; 16 ; 24 ; 32 ; 40 ; 48 ; 56 ; 84 g	NaOH = 80 g (t... a) ...a quantité théorique pour la précipitation de $Ni(OH)_2$.) water = 500 cm³
1*b* à 9*b*	$Ni(NO_3)_2, 6\,H_2O$ = 100 g water = 500 cm³	NaOH = 27 g Hypochlorite de sodium 4 N : 0,17 ; 34 ; 51 ; 68 ; 85 ; 102 ; 119 ; 170 cm³ water = 500 cm³ then : NaOH = 53 g water = 500 cm³
1*c* à 9*c*	$Ni(NO_3)_2, 6\,H_2O$ = 100 g Solution { NaOH = 0 ; 3 ; 6 ; 9 ; 12 ; 15 ; 18 ; 21 ; 30 g. water : 0 ; 10 ; 20 ; 30 ; 40 ; 50 ; 60 ; 70 ; 100 cm³. Br_2 = 0 ; 2 ; 4 ; 6 ; 8 ; 10 ; 12 ; 14 ; 20 cm³.	NaOH = 80 g water = 500 cm³
1*d* à 9*d*	NaOH = 80 g 500 cm³ water Br_2 = 0 ; 2 ; 4 ; 6 ; 8 ; 10 ; 12 ; 14 ; 20 cm³	$Ni(NO_3)_2, 6\,H_2O$ = 100 g water = 500 cm³
1*e* à 9*e*	$Ni(NO_3)_2, 6\,H_2O$ = 100 g water = 500 cm³	water = 500 cm³ NaOH = 27 ; 30 ; 33 ; 36 ; 39 ; 42 ; 45 ; 48 ; 57 g Br_2 = 0 ; 2 ; 4 ; 6 ; 8 ; 10 ; 12 ; 14 ; 20 cm³ then : NaOH = 53 g water = 500 cm³

a) three times the theoretical amount for the precipitation of $Ni(OH)_2$.

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under the following conditions:

-divergence gap and dispersion gap: $1^{o}/2$

-reception gap: 0.2mm

-velocity of goniometer operation: 1^{o} for 2θ per minute

All recordings have been started at $2\theta = 6^{o}$.

Magnetic Properties

The study of magnetic properties of these compounds, which are relatively not very stable has been effected immediately upon their preparation in order to avoid any degree of decomposition.

1. Study of magnetism at room temperature. We have used a scale of the Foëx-Forrer type (6), (7). The value of the median susceptibility is given in the formula

$$10^{6}\cdot\chi_{s} = \frac{m_{R}}{m_{s}}\cdot\frac{\chi_{s}-\chi_{a}}{\chi_{R}-\chi_{a}}\left(\chi_{R}-\frac{0{,}029}{\rho_{R}}\right)+\frac{0{,}029}{\rho_{s}}$$

- m_a and m_s are the masses of the reference material and of the studied substance. X_s, X_a and X are algebraic values of measured differences in potentials which are proportionate to the magnetic forces affecting the cup full of the substance, the cup full of the reference material and the empty cup.

χ_R is the specific susceptibility of the reference material.

ρ_R and ρ_s are, respectively, the specific mass of the solution in question and of the studied substance.

The reference substance under investigation is an aqueous solution of (approximately) 30% nickel chloride (Ref.8). The

specific susceptibility χ_R of the solution is:

$$10^6 \cdot \chi_m^v = \frac{10\,030}{T} p - 0{,}720\,(1-p)$$

p = the mass function of the $NiCl_2$ solution (about 0.3) determined by electrolysis.

T is the temperature in K degrees.

We have calculated, starting with the specific susceptibility and content of nickel in the compounds, the χ_{Ni} susceptilbilities, corresponding to one atom-gram of nickel and reduced, in all cases, the results to 25°C, assuming that the products obey the Curie law. In relation to the thermomagnetic study below, this approximation is justifiable -- within a several degrees range limit. Finally, we have established the dimagnetic correction starting with the values given in the Pascal system, or even by Selwood (Ref.8):

H_2O and O^{--}: -13.10^{-6}; Ni = -12.10^{-6}.

These corrections are small in relation to the susceptibility measured and their impredsion can play no appreciable part in the final results.

The values $\chi_{Ni}^{25°}$ thus shown in Table II are then corrected susceptibilities of diamagnetism at 25°C, of the atom-gram of nickel in nickel hydroxides with a valence of between 2 and 3.

We may state that the preceding preparations have an O_{active}/Ni relation always inferior to 0.5, in other words, the oxidation level remains always inferior to that of the trivalent nickel hydroxide, while the maximum amount of the oxidizer used

was sufficient to obtain the NiO_2 bioxide; but, once the work of Besson (Ref. 9), Glemser and Einerhand (Ref.10) are known as they relate to the stability of superior nickel hydroxides, it is only logical to conclude that a considerable decomposition in the course of the preparation has taken place, during the washing and drying of the initially formed products.

In order to expand our measurements beyond the preceding limits, we have devised a method of magnetic measuring (Ref.11) making it possible to determine the susceptibility χ_β of a precipitate β immersed in its initial liquid.

$$\chi_\beta = \frac{S}{S_R} \cdot \frac{m_R}{m_\beta} \left(\chi_R - \frac{\chi_\alpha \rho_\alpha}{\rho_R} \right) + \frac{\chi_\alpha \rho_\alpha}{\rho_\beta}$$

S = the surface in algebraic value contained between the parenthesis representing the magnetic force which affects respectively the β precipitate containing-tube in the presence of the solution α and on the same tube containing only the homogeneous phase α as a function of the relative displacement of the tube in relation to the field.

S_n = the surface measured in a manner identical to the preceding one, by replacing the α and β phases by air and water, respectively.

m_R and m_β are the respective masses of water and of the β precipitate.

χ_β, χ_α, χ_R and χ_a are the specific susceptibilities in respect to the β precipitate, the α solution, in which the precipitate is immersed, to water and to air.

ρ_β, ρ_α, ρ_R and ρ_a = the specific masses in respect to the

	Formula	$x_{Ni}^{25} \cdot 10^6$	X Spectra
1a	$NiO,1,34H_2O$	4740	
2a	$NiO_{1,071}.1,35H_2O$	4300	
3a	$NiO_{1,151}.1,40H_2O$	3770	
4a	$NiO_{1,236}.1,43H_2O$	3185	
5a	$NiO_{1,318}.1,24H_2O$	2575	
6a	$NiO_{1,380}.1,15H_2O$	2255	
7a	$NiO_{1,422}.1,12H_2O$	1930	
8a	$NiO_{1,448}.1,25H_2O$	1790	
9a	$NiO_{1,455}.1,23H_2O$	1730	
1c	$NiO,1,24H_2O$	4690	5 4 3 2 1,5 1,2
2c	$NiO_{1,094}.1,20H_2O$	4060	
3c	$NiO_{1,017}.1,15H_2O$	4585	
4c	$NiO_{1,026}.1,22H_2O$	4510	
5c	$NiO_{1,047}.1,26H_2O$	4405	
6c	$NiO_{1,029}.1,39H_2O$	4490	
7c	$NiO_{1,221}.1,23H_2O$	3180	
8c	$NiO_{1,329}.0,92H_2O$	2505	
9c	$NiO_{1,058}.1,44H_2O$	4290	5 4 3 2 1,5 1,2
1e	$NiO,1,49H_2O$	4685	
2e	$NiO_{1,122}.1,41H_2O$	3855	
3e	$NiO_{1,178}.1,33H_2O$	3420	
4e	$NiO_{1,267}.1,28H_2O$	2885	
5e	$NiO_{1,325}.1,24H_2O$	2530	
6e	$NiO_{1,357}.1,29H_2O$	2380	
7e	$NiO_{1,404}.1,49H_2O$	2200	
8e	$NiO_{1,361}.1,31H_2O$	2415	
9e	$NiO_{1,464}.1,51H_2O$	1825	

	Formula	$x_{Ni}^{25} \cdot 10^6$	X Spectra
1b	$NiO,1,86H_2O$	4720	
2b	$NiO_{1,086}.1,52H_2O$	4225	
3b	$NiO_{1,170}.1,22H_2O$	3560	
4b	$NiO_{1,251}.1,16H_2O$	3010	
5b	$NiO_{1,310}.1,02H_2O$	2615	
6b	$NiO_{1,332}.1,11H_2O$	2450	
7b	$NiO_{1,362}.1,25H_2O$	2365	
8b	$NiO_{1,382}.1,16H_2O$	2210	
9b	$NiO_{1,393}.1,52H_2O$	2170	
1d	$NiO,1,13H_2O$	4680	
2d	$NiO_{1,027}.1,32H_2O$	4570	
3d	$NiO_{1,091}.1,14H_2O$	4085	
4d	$NiO_{1,114}.1,23H_2O$	3955	
5d	$NiO_{1,118}.1,16H_2O$	3890	
6d	$NiO_{1,179}.1,19H_2O$	3480	
7d	$NiO_{1,255}.0,95H_2O$	2965	
8d	$NiO_{1,154}.1,11H_2O$	3620	
9d	$NiO_{1,231}.1,26H_2O$	3135	
			5 4 3 2 1,5 1,2
	$Ni(OH)_2$ [10]		
	$Ni_3O_2(OH)_4$ [10]		
	$Ni_3O_2(OH)_4$ [13]		
	$\beta NiOOH$ [10]		

TABLE II. Superior hydroxides of nickel prepared by the wet (humid) method.

preceding compounds.

Or also:

$$\chi_{Ni} = \frac{S}{S_R} \cdot \frac{m_R}{n} \left(\chi_R - \frac{\chi_\alpha \rho_\alpha}{\rho_R} \right) + \frac{M \chi_\alpha \rho_\alpha}{\rho_\beta}$$

formula in which M (the molecular mass of the precipitate) and n (number of atom-grams of Ni contained in the precipitate) are connected by the relation:

$$m = n.M$$

being the magnetic susceptibility of the precipitate. This susceptibility has not been freed of dimagnetism, but reduced to 1 atom-gram of nickel.

Now, inasmuch as

$$\chi_R = -0{,}720.10^{-6} \quad \rho_R = 1$$
$$\chi_\alpha \rho_\alpha = \chi_\alpha = 0{,}028.10^{-6}$$
$$\chi_\alpha \rho_\alpha = \chi_\alpha = -0{,}75.10^{-6} \text{ approximately}$$
$$M = 100 \text{ approximately}$$
$$\rho_\beta = 4 \text{ approximately}$$

These three last values, although approximate, may be utilized in the preceding formula, inasmuch as the expression $\frac{M \chi_\alpha \rho_\alpha}{\rho_\beta}$ is very weak in relation to χ_{Ni}.

From where, finally:

$$10^6 \cdot \chi_{Ni} = -0{,}748 \frac{S}{S_R} \cdot \frac{m_R}{n} - 20$$

Precipitation has been achieved in a measuring tube by adding successively to a 1 cu cm solution of $Ni(NO_3)_2, 6H_2O$ (0.327 M/liter), an increasing amount of an oxidizing solution (persulfate

hypochlorite, or hypobromite of sodium), 2 cu cm of NaOH(5 N) and 5 cu cm of water. Upon a rest period of several hours -- in order to enable the precipitate to assemble by decantation according to a level not to exceed the homogeneity zone of the magnetic field of the electromagnet -- magnetic measures are effected by displacing the mobile magnet to avoid modifying the distribution of the precipitate in the tube. These displacements are measured by observing through an interlocked glass (viewer) of the magnet a millimetric scale placed on the measuring tube.

Immediately upon magnetic measuring, the solution swimming on the surface is removed by means of a syringe and we evaluate its oxidizing capacity. The latter is generally equal to zero, as the precipitate decomposes the excess of the oxidizing solution. The precipitate is then directly dissolved in SO_4H_2 N/10 in the presence of KI. The active oxygen is proportioned iodometrically, by means of a solution of sodium N/50 hyposulfite. However, when the amount of the used oxidizer is quite considerable, the solution swimming on the surface remains slightly oxidizing and the precipitate, prior to dissolution, is then subjected to a rapid washing with a solution of the N sodium hydroxide. The nickel content has been initially determined by weighing the amount of the titrated solution of nickel nitrate used. The results that we obtained by this method are assembled and presented in Table III where $\chi^{25°}_{Ni}$ is, as before, the corrected susceptibility of the diamagnetism at 25°C, of the atom-gram of nickel in the corresponding compounds.

Table III

Magnetic Susceptibilities of Superior Nickel Hydroxides Prepared in the Magnetic Measuring Tube

Oxidation by sodium persulfate.		Oxidation by sodium hypochlorite		Oxidation by sodium hypobromite.	
$\frac{O_{actif}}{Ni}$	$\chi^{25°}_{Ni} \cdot 10^6$	$\frac{O_{actif}}{Ni}$	$\chi^{25°}_{Ni} \cdot 10^6$	$\frac{O_{actif}}{Ni}$	$\chi^{25°}_{Ni} \cdot 10^6$
0	4 740	0	4 765	0	4 755
0,120	3 890	0,108	4 040	0,143	3 875
0,241	3 050	0,209	3 420	0,248	3 245
0,349	2 220	0,216	3 445	0,353	2 585
0,410	1 895	0,269	3 100	0,488	1 940
0,472	1 550	0,320	2 895	0,553	1 430
0,472	1 525	0,425	2 315	0,653	1 180
0,507	1 405	0,444	2 135	0,720	905
0,580	1 195	0,545	1 545	0,726	925
0,658	950	0,680	1 035		
0,695	900	0,741	885		
0,711	840				
0,716	900				
0,710	910				

2. THERMOMAGNETIC STUDY

This study has been achieved in a helium atmosphere -- in a vacuum the samples could have undergone decomposition and a considerable dehydration -- by means of an installation (Ref.12) designed and built in the laboratory, and to which we have added certain alterations, in order to adapt it to our measurements, as follows:

- The tube made of glass and forming the inferior part of the column carries a double coil in the opposite direction and provided with close-wound turns and this winding is covered with an adhesive tape and fed an alternating current. In this manner we achieve a uniform heating while annulling, at any moment, the stray field created by the coil.

- Helmhotz coils at a distance superior to the beam are

placed against the pole parts of the magnet in such a manner that their axis is situated at the level of the cup during the measurements, in other words, at the height of the maximum field gradient. They create a field with an opposite direction to that of the electromagnet and modify (in the horizontal direction) the distribution of lines of force in such a manner that the cup is no longer attracted to the parts of the pole.

The results of measurements on the b and e series are presented in Table IV.

TABLE IV

Thermal variation of Magnetic Susceptibility of Superior Nickel Hydroxides.

1b		2b		3b		4b		5b		6b		7b		8b		9b	
T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$
77	23 110	77	21 500	77	16 960	77	14 800	77	12 520	77	11 740	77	11 600	77	10 510	77	10 340
104	15 520	106	13 460	107	10 605	101	9 930	100	8 550	105	7 015	100	7 845	101	6 940	100	7 030
126	12 310	124	11 130	127	8 735	123	7 750	118	6 900	128	5 550	119	6 140	117	5 700	108	6 470
148	10 090	143	9 295	148	7 485	140	6 590	126	6 345	151	4 595	149	4 770	149	4 435	129	5 160
166	8 885	164	7 965	187	5 720	156	5 810	153	5 200	171	4 040	183	3 860	183	3 590	152	4 270
194	7 500	184	7 070	230	4 680	190	4 755	188	4 180	193	3 565	213	3 300	214	3 075	182	3 560
212	6 755	219	5 910	261	4 085	226	3 995	213	3 645	228	3 070	250	2 845	249	2 660	218	2 960
234	6 065	255	5 090	291	3 630	260	3 440	237	3 285	267	2 670	293	2 400	293	2 245	265	2 430
257	5 515	288	4 425			295	3 015	271	2 865	295	2 410					286	2 250
288	4 820	292	4 360					293	2 660								

1e		2e		3e		4e		5e		6e		7e		8e		9e	
T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$
77	23 410	77	19 420	77	16 630	77	14 150	77	11 910	77	11 340	77	10 150	77	11 010	77	7 380
103	15 380	101	12 630	105	10 560	94	10 360	100	8 030	99	7 690	103	6 540	104	6 960	98	5 340
130	11 420	127	9 730	130	8 270	119	7 720	120	8 500	123	5 900	125	5 190	123	5 650	118	4 310
154	9 550	150	7 990	154	6 810	144	6 210	122	6 430	146	4 870	142	4 440	143	4 750	141	3 570
182	7 990	154	7 740	183	5 650	171	5 080	145	5 190	171	4 090	161	3 900	161	4 200	159	3 160
217	6 590	183	6 440	215	4 740	197	4 400	177	4 190	204	3 430	181	3 490	182	3 760	178	2 880
256	5 460	213	5 470	254	4 020	203	4 290	204	3 610	244	2 880	221	2 860	220	3 140	215	2 440
296	4 705	253	4 580	295	3 450	238	3 640	245	3 040	294	2 405	253	2 535	258	2 750	251	2 110
		292	3 940			291	2 960	290	2 600			290	2 255	294	2 440	293	1 860

EXPLAINING THE RESULTS AND DISCUSSION

1. An X-Ray Investigation.

The action of oxidizing agents, such as the persulfate, hypochlorite or hypobromite of sodium upon $Ni(OH)_2$ results in nickel hydroxides with valences superior to 2, according to prior results. In the compounds prepared by the classical method (Table II), the relation of O_{active}/Ni (Table III) reach a degree of oxidation corresponding to a relation of O_{active}/Ni in the neighborhood of 0.75 which is equivalent to a mixture in equal proportions of Ni(III) and Ni (IV). We can then state that the nickel valence in superior hydroxides can be greater than 3. This result would tend to be in favor of the existence of a nickel compound with four valences, a fact still disputed at present.

The method to be used in preparation is by no means indifferent. We can see, in fact, that in the c and d series the oxidation degree of the compounds does not increase in the same manner as it does in other series depending on growing amounts of added oxidizers. This fact is explained by the fact that the oxidizer found in the nickelous solution has undergone a considerable catalytic decomposition at the contact with the first granules of the precipitate. Yet, this effect is considerably less pronounced in persulfate.

An investigation using X-rays permits us to establish that since the start of oxidation the 102 ray of $Ni(OH)_2$ (d = 1.75 Å)

decreases in intensity before it disappears completely (Table II), while the other rays become larger. Also, the rays d = 2.63Å and d = 2.40 Å approach one another, taking up positions which correspond to the spectrum of $Ni_3O_2(OH)_4$, and, finally, the rays d = 1.56 Å and d = 1.48 Å are displaced toward small angles, while the ray d = 2.63 Å disappears completely and the reticular distance corresponding to ray d = 4.60 Å increases its value. The diagram then approaches that of NiOOHβ. We thus establish a continuous evolution of $Ni(OH)_2$ toward NiOOHβ, passing through the intermediate stage $Ni_3O_2(OH)_4$, amd not a mixture of different components, which would make their own rays appear. Such interpretation shows the validity of the Bode theory (Ref. 14), who thinks that the passage of $Ni(OH)_2$ to NiOOH is effected within one single phase $NiO_x(OH)_{2-x}$ where x varies from 0 to 1, with, however, a superior limit capable of reaching a value greater than 1. In the a series an anomaly appears in the spectra of samples the most oxidized: the disappearance of the ray d = 4.84 Å corresponds to the reflection on the plan of the base. The spectrum then corresponds to that of NiOOH which has already been obtained by Glemser and Einerhand (Ref.10) by action of an alkaline solution of persulfate upon a solution of $K_2(Ni(CN)_4)$. The persulfate thus seems to act in a different way from other oxidizers. This phenomenon is confirmed by means of magnetic measurements.

2. Magnetic Study at Room Temperature.

Magnetic measurements at room temperature show that susceptibility

gradually decreases as the oxidation degree increases (Fig.I). At the beginning of oxidation, all points will be lining up in good agreement along a single straight line, whatever the oxidizer used. In hydroxides, on the contrary, the most oxidized the points will be displaced from the initial line. The compounds obtained through the persulfate action have, nevertheless a susceptibility weaker than those prepared starting with other oxidizers. This phenomenon is found in a still more pronounced manner in Fig. 2 in the measurements effected on the components immersed in the initial liquid where thepoints relating to oxidation by persulfate are situated on a quite distinct curve right after the start of oxidation.

How can we connect the variations of magnetic susceptibility with the oxidation degree of superior nickel hydroxides?

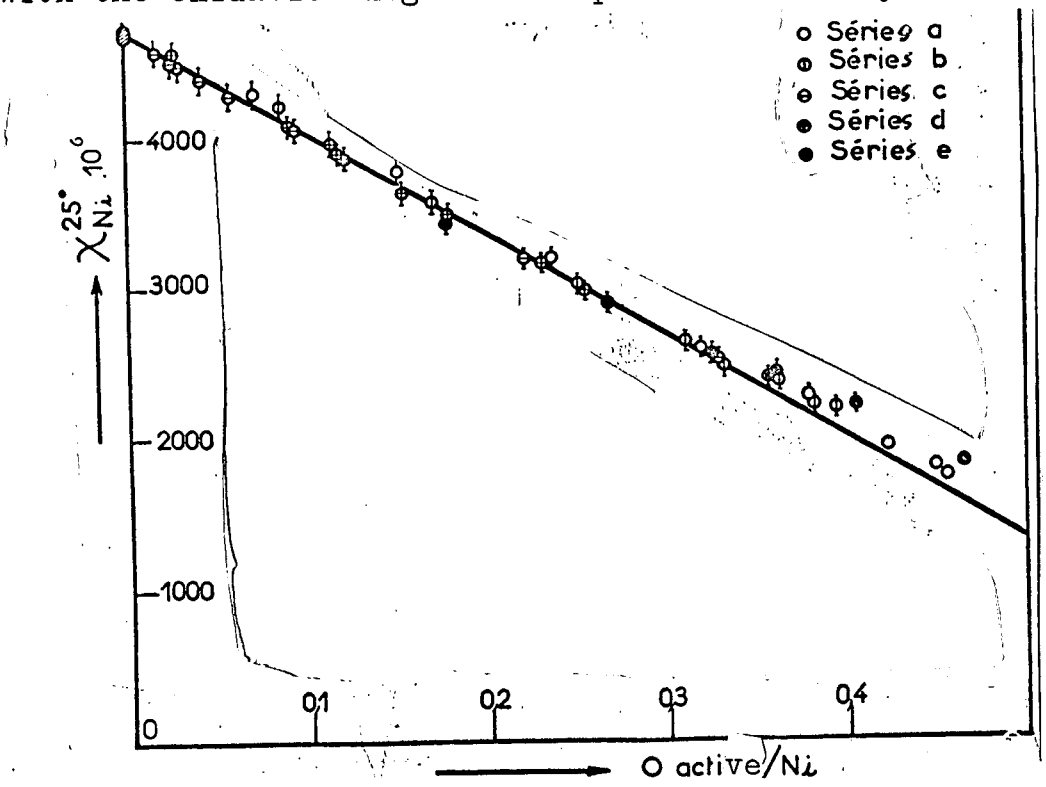


Fig. 1. Relation between magnetic susceptibility and the oxidation degree of superior nickel hydroxides.

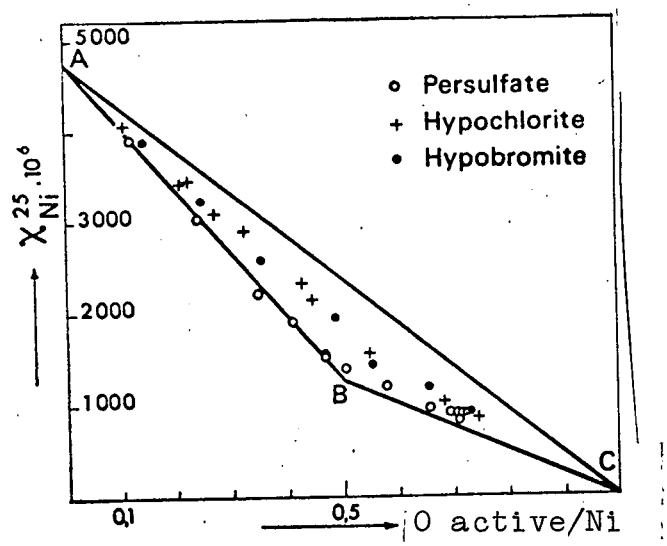
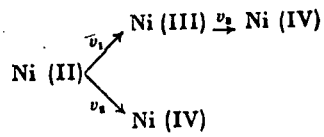


Fig. 2. Relation between the magnetic susceptibility and the oxidation degree of superior nickel hydroxides prepared in the magnetic measuring tube.

We can present a schematic expression for the oxidation of $Ni(OH)_2$ in superior hydroxides in the following manner:



ν_1, ν_2 and ν_3 being respectively, the velocities of oxidation of Ni (II) into Ni (III) and Ni(IV), and of Ni (III) into Ni (IV).

a) v_2 and v_3 are negligible values in relation to v_1. Ni (II) is then oxidized into Ni (III), then into Ni (IV). For a compound with relation O_{act}/Ni comprised between 0 and 0.5, $\chi^{25°}_{Ni}$ must then vary linearly depending upon the degree of oxidation.

When oxidation is continued beyond Ni (III) the crystal then comprises ions of Ni (III) and Ni (IV), and $\chi_{Ni}^{25°}$ must, as before, vary linearly depending upon the relation O_{act}/Ni with, however, a different gradient as the susceptibility is not in proportion with the number n of electrons nonpaired with ions but paired with the n (n + 2). In this hypothesis, the curve connecting $\chi_{25°}^{Ni}$ to O_{act}/Ni must present itself as a straight broken line whose angular point is found at $O_{act}/Ni = 0.5$.

b) v_2 and v_3 are comparable to v_1. The substance is then composed of Ni (II), Ni (III) and Ni (IV). For analogous relation of the O_{act}/Ni, the $\chi_{Ni}^{25°}$ may then have different values according to the proportion of the cations in different ionization states, yet they should always be superior to the value corresponding to the hypothesis (a). The experimental points must, nevertheless, be situated within the ABC triangle (Fig.2), with summits corresponding to respective susceptibilities of Ni (II), Ni (III) and Ni (IV) as experimentally measured or obtained by extrapolation.

Hypothesis (a) permits a good interpretation of results relating to hydroxides subjected to persulfate action, while -- on the contrary -- those subjected to the action of hypochlorite or hypobromite of sodium confirm the second hypothesis, (Fig.2). These conclusions are in perfect agreeement with the fact that persulfate is quite clearly the less strong oxidizer of all oxidizers used by us.

Hydroxides whose susceptibilities have been described in Fig. 1 have been subjected to a prolonged washing and drying which

have considerably decomposed the initial products of formation and, first of all the Ni(IV) has been reduced to Ni (III). It is not surprising, therefore, that all points are situated on the same line in conformance with the first interpretation, whatever the utilized oxidizer may be.

We can experimentally determine -- on the precipitate -- the average magnetic susceptibility χ of an atom-gram of nickel and the relation $O_{act}/Ni = \alpha$. If a, b and c are, respectively, atomic fractions of Ni (II), Ni (III) and Ni (IV) of respective atomic susceptibilities χ_1, χ_2, χ_3, it appears that

$$\left.\begin{aligned} a+b+c &= 1 \\ a\chi_1 + b\chi_2 + c\chi_3 &= \chi \\ \frac{b}{2} + c &= \alpha. \end{aligned}\right\}$$

whereforeom

$$\left.\begin{aligned} a &= \frac{(1-\alpha)(2\chi_2 - \chi_3) - \chi}{2\chi_2 - (\chi_1 + \chi_3)} \\ b &= \frac{2[\chi - \chi_1 + \alpha(\chi_1 - \chi_3)]}{2\chi_2 - (\chi_1 + \chi_3)} \\ c &= \frac{\chi_1 - \chi + 2\alpha(\chi_3 - \chi_1)}{2\chi_2 - (\chi_1 + \chi_3)} \end{aligned}\right\}$$

or again, by replacing χ_1, χ_2 and χ_3 by their values experimentally established in a direct manner or by extrapolation ($\chi_1 = 4\,720.10^{-6}, \chi_2 = 1\,320.10^{-6}, \chi_3 = 0$) (Fig. 1 and Fig. 2):

$$\left.\begin{aligned} a &= \frac{\chi.10^6 - 2\,640\,(1-\alpha)}{2\,080} \\ b &= \frac{4\,720\,(1-\alpha) - \chi.10^6}{1\,040} \\ c &= \frac{\chi.10^6 + 6\,800\alpha - 4\,720}{2\,080}. \end{aligned}\right\}$$

The calculation of a, b and c makes possible the determination of proportions according to which the nickel is engaged in various states of valences.

As an example we have performed the computation for three samples taken at random from Table III.

α	$\chi^{25°}_{Ni} \cdot 10^6$	a	b	c
0,320	2 895	0,53	0,30	0,17
0,545	1 545	0,17	0,58	0,25
0,741	885	0,10	0,32	0,58

3. Magnetic Research Depending Upon Temperature.

Transition elements with an incomplete layer 3 d form compounds possessing paramagnetic properties of molecular susceptibility corrected of dimagnetism.

$$\chi_M = \frac{N\mu^2}{3k(T-\theta)} = \frac{Np_{eff}^2\mu_B^2}{3k(T-\theta)} = \frac{C}{T-\theta}$$

with

$$C = \frac{N\mu_B^2 p_{eff}^2}{3k}.$$

Whereforem:

$$p_{eff} = \sqrt{\frac{3k}{N\mu_B^2}} \cdot \sqrt{C} = 2{,}84\sqrt{C}$$

N = the Avogadro number

μ = magnetic moment of the molecule

k = Boltzmann constant

T = temperature in K degrees

θ = Curie temperature

p_{eff} = effective magnetic moment of the molecule in Bohr magnetons

β_B = Bohr magneton

C = Curie constant

The curve representing the function $1/\chi = f(T)$ is then a straight line with a gradient I/C and an abscissa with the origin at θ.

The interaction of neighboring ions produces the following effect: it introduces an assymetric alactrostatic field which provokes the blocking of orbital moments of the 3 d electrons without influencing their moment of spin (Ref. 15). Therefore:

$$p_{eff} = \sqrt{4S(S+1)}$$

instead of:

$$p_{eff} = \sqrt{L(L+1) + 4S(S+1)}.$$

This last formula is applied to a paramagnetic gas in which particles are not affected by electric and magnetic fields of their neighbors. In solids, the internal fields of the crystal play a part more important yet, than in solutions and substances in general do not, any longer, follow the Curie law but obey the Curie-Weiss law which introduces the supplementary parameter θ.

As a matter of fact, the experimental values of p_{eff} show that often the orbital moment is only partially blocked. This is unusual for compounds which make ions of the second half of transition elements intervene. To these elements belongs nickel.

In fact, we have established for $Ni(OH)_2$:

p_{eff}= (p_{eff} theoretical for a single spin = 2.83 μ_B)

θ = 21°K.

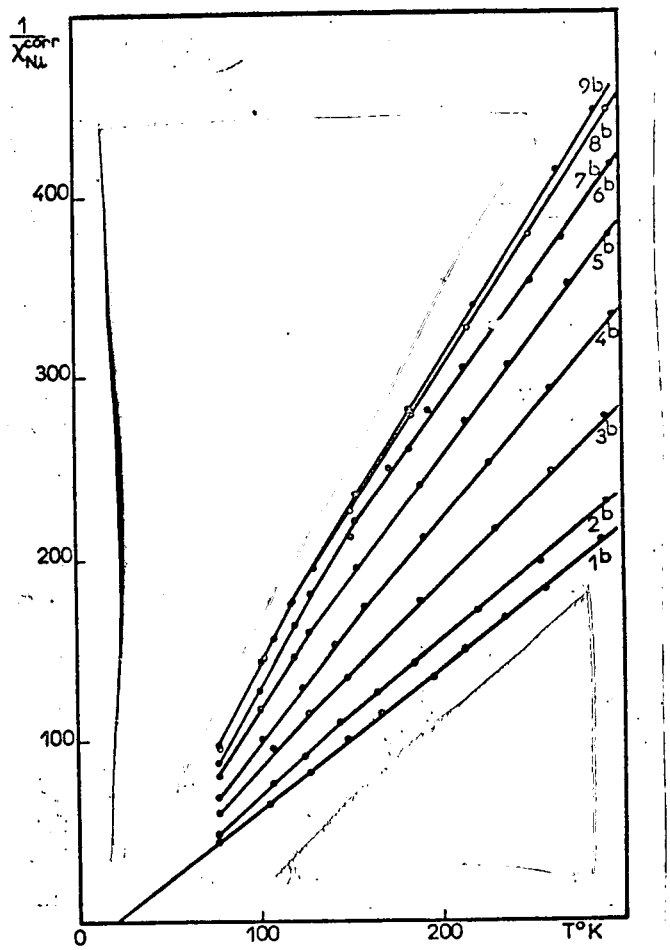


Fig. 3. Thermomagnetic Study of Samples of the b Series.

On the other hand, Figs. 3 and 4 relating to the thermomagnetic investigations of samples show a curvature, quite pronounced, of the straight line $1/\chi = f(T)$.

a) This could be due to a mixture of Ni (III) with Ni (II) in the compounds studied. If χ_1 and χ_2, C_1 and C_2, θ_1 and θ_2 are, respectively, atomic susceptibilities, the Curie constants and the Curie temperatures of Ni (III) and Ni (II) in the range of temperatures studied: $\chi_1 = \frac{C_1}{T - \theta_1}$ and $\chi_2 = \frac{C_1}{T - \theta_2}$.

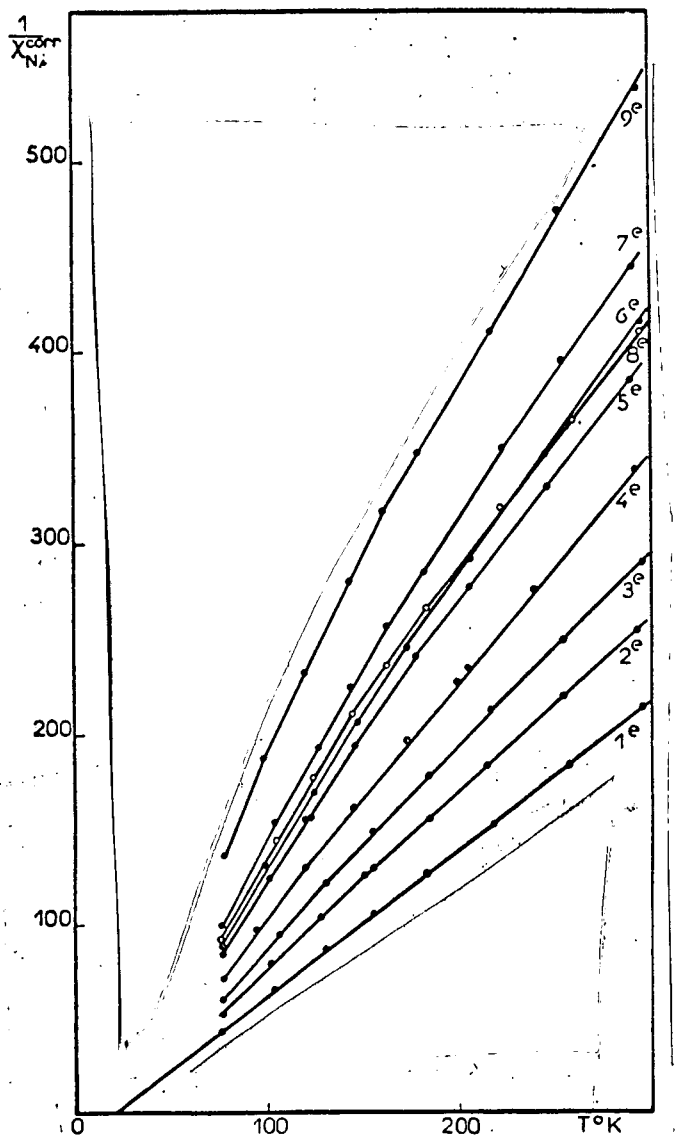


Fig. 4. Thermomagnetic Investigation of Samples from Series e

Their mixture, according to atomic fractions x and 1 - x has a susceptibility such as to show:

with

The study of this function within the range where it has a physical direction results in a curve (C) (Fig.5) with a curvature effectively pointing out in the same direction as that in Figs. 3 and 4.

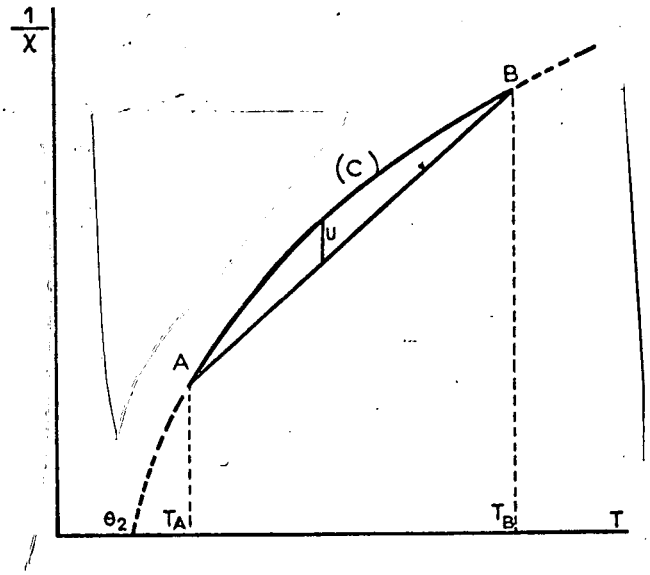


Fig. 5. Representative Curve of the function $\frac{1}{\chi} = \frac{(T-\theta_1)(T-\theta_2)}{aT-b}$.

The intersection of (C) with the temperature axis takes place -- for the highest value of θ. We state that the beams of the experimental curves are convergent toward $\theta_2 = 21^{\circ}K$ of $Ni(OH)_2$ and therefore $\theta_1 \leq \theta_2$.

The maximum divergence u between the curve (C) and the secant AB (Fig.5) corresponds to:

$$T = \theta_1 + m\alpha + \sqrt{T'_A T'_B}$$

and has a value of:

$$u = \frac{m(1-m)\alpha^2\left(\sqrt{T'_A} - \sqrt{T'_B}\right)^2}{\alpha T'_A T'_B}$$

by expressing:

$$m = \frac{C_1 x}{C_1 x + C_2(1-x)}$$

$$\alpha = \theta_2 - \theta_1$$

$$T'_A = T_A - \theta_1 - m\alpha$$

$$T'_B = T_B - \theta_1 - m\alpha$$

Calculation then shows that if we take C_1 equal to 0.372 (theoretical value for a compound possessing an unpaired electron), u is negligible* within the limits of precision of our measurements and can not be experimentally detected in the course of a thermal variation in the 700 to 300°K range for θ values comprised between 20°K and -50°K. In order to obtain divergences comparable to those that we have observed, θ_1 should be inferior to -100°K which seems to be rather unreal. We shall give, at a later time, an order of magnitude for θ_1 which is far more satisfying.

b) Cabrera and Duperier (Ref.17) and Miss Serres (Ref. 18) during their studies on the magnetism of chlorides and sulfates of nickel have already explained analogous divergences using the Weiss law, by existence of a constant paramagnetism a superimposed to the variable paramagnetism connected with the temperature, and have suggested the following variation law:

---

*) A thermomagnetic study performed on an equimolecular mixture of $Ni(OH)_2$ and $CuCl_2$, 2 H_2O (p_{eff} = 1.9μB', θ = -5°K (Ref. 16)) shows effectively a perfect linearity of the curve $1/\chi = f(T)$ with abscissa having an origin equal to 21°K.

$$\chi - a = \frac{C}{T - \theta}$$

This correction, however, does not make possible the rectification of the experimental curves into one straight line, but rather into two less definite portions of a straight line. We should then admit the existence of two different magnetic states according to the range of the considered temperatures.

c) Rather than assume such a discontinued variation p_{eff} at a certain temperature, it would seem more logical to think, as Van Vleck (Ref.15) that there is a continuous variation of the magnetic moment inasmuch as the blocking condition of the orbital moment which is connected with temperature should then be better achieved at a low temperature, which, in turn, requires an increase in the observed moment depending on the temperature.

Each sample being considered as a mixture of Ni (III) and Ni (II), its susceptibility is equal to:

$$\chi = x\chi_1 (1 - x)\chi_2$$

The determination of the gradient of the tangent of the experimental curves at the lowest temperature on our scale (77°K) makes possible the calculation of a magnetic moment p relative to each compound which can be connected to the magnetic moments p_1 and p_2 of Ni(III) and Ni(II) by*:

*) We have assumed here that, in the first approximation, the intersection point of the tangent and the curve $1/\chi = f(T)$ with the axis of temperatures is identical with θ_2.

$$\frac{p^2}{T-\theta_2} = x\frac{p_1^2}{T-\theta_1} + (1-x)\frac{p_2^2}{T-\theta_2}.$$

Wherefrom:

$$p^2 = x\left(p_1^2\frac{T-\theta_2}{T-\theta_1} - p_2^2\right) + p_2^2.$$

For x = 1 (Ni (III) pure):

$$p_2 = p_1^2\frac{T-\theta_2}{T-\theta_1}.$$

Figure 6 brings the values of p^2 measured at a low temperature depending on the x. We find a straight line, conforming with the prior calculations and the extrapolation of x = 1 results in:

$$p_1^2\frac{T-\theta_2}{T-\theta_1} = 2{,}6$$

Wherefrom:

$$p_1^2\frac{56}{77-\theta_1} = 2{,}6.$$

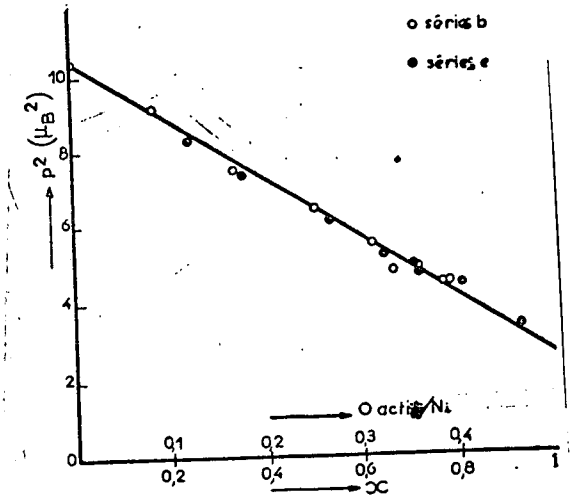
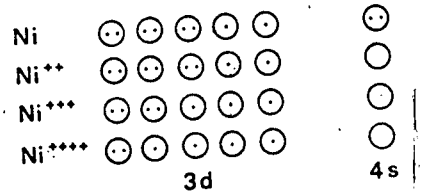


Fig. 6. Relation between p^2 and the oxidation degree of samples in the b and e series.

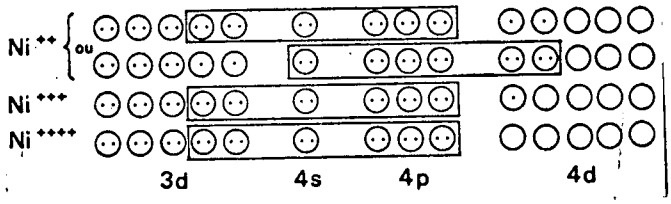
This unique relation between p_1 and θ_1 does not provide for their exact determination. However, inasmuch as each magnetic moment is, generally, a neighbor of the single spin moment, it is then possible to establish the order of magnitude of θ_1.

We shall later demonstrate that Ni(III) can have only 3 or 1 unpaired electrons. In the first case, the theoretical value of $p_1 = \sqrt{15}\,\mu_B$, would correspond to the unlikely value of $\theta_1 = -260^\circ K$ and the results at room temperature which could be obtained for mixtures of Ni(II) and Ni(III) would not conform with reality. In the second case, on the contrary, the theoretical value of $p_1 = \sqrt{3}\,\mu_B$, the corresponding value of θ_1 would be in the neighborhood of $10^\circ K$ and we again meet the results of experiments obtained at room temperature if we admit a slight orbital contribution to the measured magnetic moment when the temperature increases. We could then draw the conclusion that Ni(III) possesses only one unpaierd electron, and according to Fig. 2 we may assume that Ni(IV) should be diamagnetic in the studied compounds.

The magnetic measures have demonstrated that NiOOHβ possesses only one unpaired electron and that when oxidation is continued toward Ni(IV) the paramagnetic susceptibility becomes zero at the limit. We may believe, in considering the scheme below that the magnetic moment should grow together and at the same time as the degree of oxidation, inasmuch as Ni^{+++}, Ni^{++} and Ni^{++++} possess respectively, 2, 3, and 4 unpaired electrons.



It is, then, impossible to envisage such a structure. It should be, on the contrary, considered that nickel will share its electrons with anions O^{--} and OH^{-} and the magnetic moment of the compound will depend upon the type of coordination. Since the articles of Glemser and Einerhand (Ref 10) we know that the NiOOHβ has a hexagonal structure of the CdI_2 type, as $Ni(OH)_2$, with cations occupying the half of the octahedral holes formed by the anions. It is also well known that these layered structures always favor liasons of a covalent nature. Yet, the 6-octahedral coordination complex causes the intervention of the orbitals d^2sp^3. It would then be possible to assume that the OH^- or O^{--} ions having their positions $2p^6$ complete, would engage a dipole in each of the three neigbor atoms of nickel presenting the configuration given below:



When the orbits d^2sp^3 have been occupied by electrons, Ni(III) and Ni(II) contain, respectively, 1 and 2 electrons more than can be distributed in the three 3d orbits available. It is not known whether these supplementary electrons are repelled onto the orbit 4 d or 5 s, but as the octahedral complex of Ni(II) causes the intervention of the 4 d and 5 s orbits and the parameter a of the

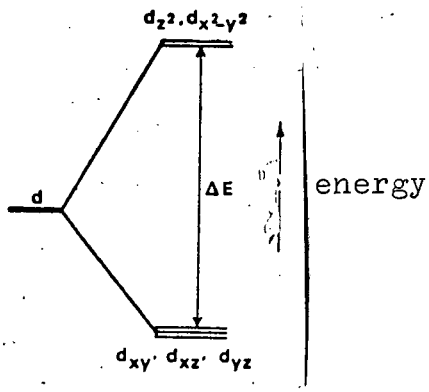
elementary hexagonal lattice of $Ni(OH)_2$ decreases during oxidation showing, in this manner, a diminishing of the octahedral covalent beam of Ni(III) in relation to that of Ni(II) -- it is probable that the configuration using the 4 d orbits for Ni(III) are exact.

The most electronegative ions, such as OH^- and O^{--} favor the formation of complexes with external orbits inasmuch as they concentrate electrons around themselves: this fact corresponds to the representation given by us for $Ni(OH)_2$. The increased electronegativity of Ni^{3+} and Ni^{4+} causes, on the contrary, a strong attraction for electrons of the anions with a subsequent formation of compounds with internal orbitals and, consequently, a decrease in the observed paramagnetism.

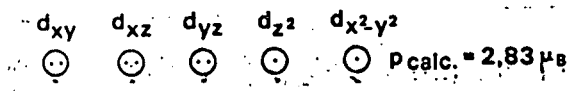
Let us determine more precisely the structure by means of the theory of the crystalline field of coordinates or of the crystalline fields, or the theory of the crystalline field. This theory is essentially based on the fact that the five 3 d orbitals degenerated in the gaseous metal ion become different in the presence of an electrostatic field due to the crystalline field.

Thus in the case of an octahedral complex, the position of the various levels of energy in relation to the 3 d orbitals is represented in the Fig. below where ΔE is the energy difference between the superior and inferior levels. The orbitals d_z, $d_{x^2-y^2}$ where energies increase in relation to orbitals d_{xy}, d_{xz} and d_{yz}, will have the electronic filling effected in the following manner: the first three electrons occupy the series d_{xy}, d_{xz}, and d_{yz}, will

have the electronic filling effected in the following manner: the first three electrons occupy the series d_{xy}, d_{xz} and d_{yz} where the energy is the lowest. Then the supplementary electrons will occupy either the orbitals d_z and $d_{x^2-y^2}$ if the enrgy of electronic pairing is superior to ΔE (crystalline field quite weak), or will be paired in the orbitals d_{xy}, d_{xz} and d_{yz} if ΔE is superior to the pairing energy of two electrons (strong crystalline field).

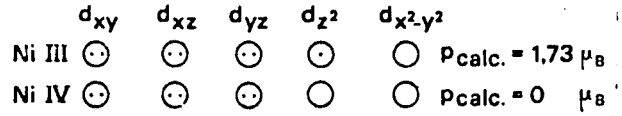


$Ni(OH)_2$ with a d^8 configuration may then be represented in the following manner:



whatever the force of the crystalline field may be. The position given for OH^- in the spectrochemical series or that of Fajans-Tsuchida, it is probable that ΔE is actually inferior to the electron pairing energy. However, for a NiOOH Ni(III) and a fortiori for Ni(IV) the preceding inequality must change the direction

as ΔE has an approximately double value for a trivalent ion as compared to a bivalent ion.



This hypothesis which accounts for the abnormal magnetic behavior of nickel in the state of valence greater than 2 should, certainly, be subjected to an expeimental confirmation by measuring the energy ΔE of the division of orbitals d in two halves by determining the absorption frequencies in the visible and the ultraviolet, truly difficult to achieve in the solids.

SECOND PART

Crystallographic and Magnetochemical Study of Oxides and Hydroxides of Nickel Prepared by the Dry Method

Simultaneously with the investigations effected by the wet method, numerous authors have tried to obtain superior anhydrous nicke oxides by the dry method, particularly starting with $Ni(NO_3)_2$, $6H_2O$. Having found profound divergences between the results obtained (Ref.1) we have undertaken a magnetochemical investigation of the thermal decomposition of $Ni(NO_3)_2$, $6H_2O$ in a vacuum and in open air. We have also prepared $NiOOH_\gamma$...

Decomposition of $Ni(NO_3)_2$, $6H_2O$ in a Vacuum

1. Method of Operation.

First of all, we have used a thermobalance consisting essentially of a spiral in metal to which a micrometer is suspended and a container comprising the substance studied. The latter is placed in the center of an oven, moving vertically, and is subjected to a variety of weights during the decomposition process which modifies the length of the spiral and causes the displacement of the micrometer which we watched through a looking glass. With continuous heat conditions of 150° per hour, the thermogravimetric curve recorded is presented in Fig.7.

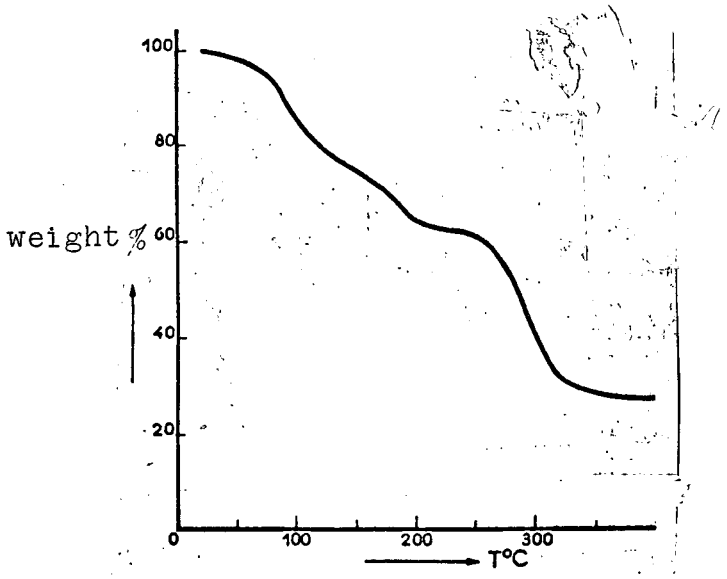


Fig.7. Thermogravimetry (150°per hr.) of $Ni(NO_3)_2$, $6H_2O$ in a vacuum.

In order to achieve a better distinction of the different levels we have also studied the effects of slow and interrupted heating of 10^{o} per day (Fig.8).

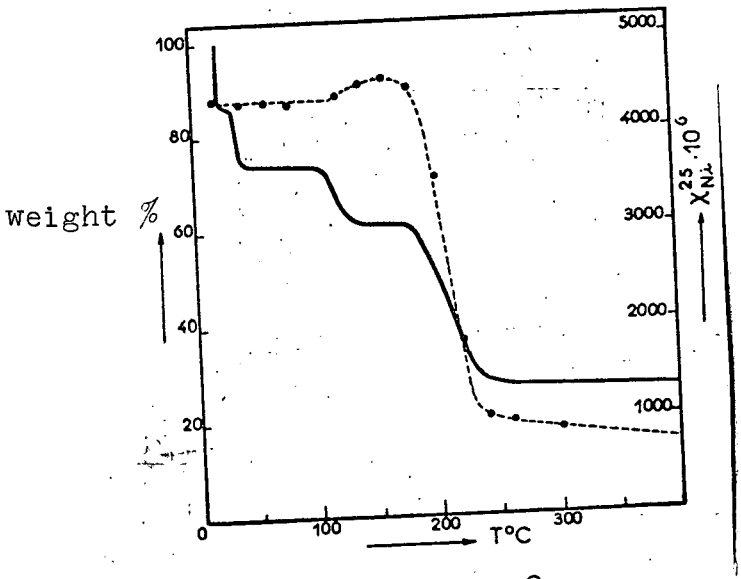


Fig.8. Thermogravimmetry (10^{o} per day) and magnetic susceptibility of $Ni(NO_3)_2$, $6H_2O$ in a vacuum.

Finally we have treated a considerable amount of nitrate according to this last method of heating, first investigating in a vacuum, and later in an electric furnace, and we have studied different samples at various temperatures, these samples were analyzed, X-rayed, and their magnetic properties have been measured.

2. Analysis.

The nickel has been apportioned by electrolysis as in the preceeding work, the content of NO_3^- has been evaluated by the classical method of Kjeldahl (reduction of NO_3^- into NH_3 by the Dewarda blending with the solution of potassium present). The water was apportioned by the Karl Fischer method. The installation

used was a water and airtight titremeter (automatic) of Prolabo with one burette equipped with electromagnetic valve. Finally, the determination by iodometry of the oxidizing capacity of the samples with low solubility studied at a temperature higher than 180° has been achieved in an inert atmosphere (argon) in the installation which is presented in Fig. 9 inspired by an article of Dyer, Borie and Smith (Ref. 19). After inserting the parts of the installation in an argon atmosphere we pour from the bromine vessel a solution of HCl(6N) which has been first degassed in the erlenmeyer which contains the sample and 1 gr of KI. Upon dissolution the excess acid is partially neutralized by a solution of NaOH(N) and the iodine is freed and apportioned by a titrated hyposulfite solution.

The spectra of X-rays h ve been achieved under identical conditions to those described in the first part of the article.

The results obtained are presented in Table V. We have not mentioned, however, the content of active O as only the samples I to O are slightly oxidizing, the relation O_{act}/Ni does not exceed 0.035, which is the maximum value obtained for the sample K.

3. Magnetic Properties.

The magnetic susceptibilities at room temperature (Table V and Fig. 8) and between 77°K and room temperature (Table VI) have been measured and the calculations have been made in the same manner as for the superior hydroxides of nickel (diamagnetic corr-

ection for NO_3^- = -14 · 10^{-6}).

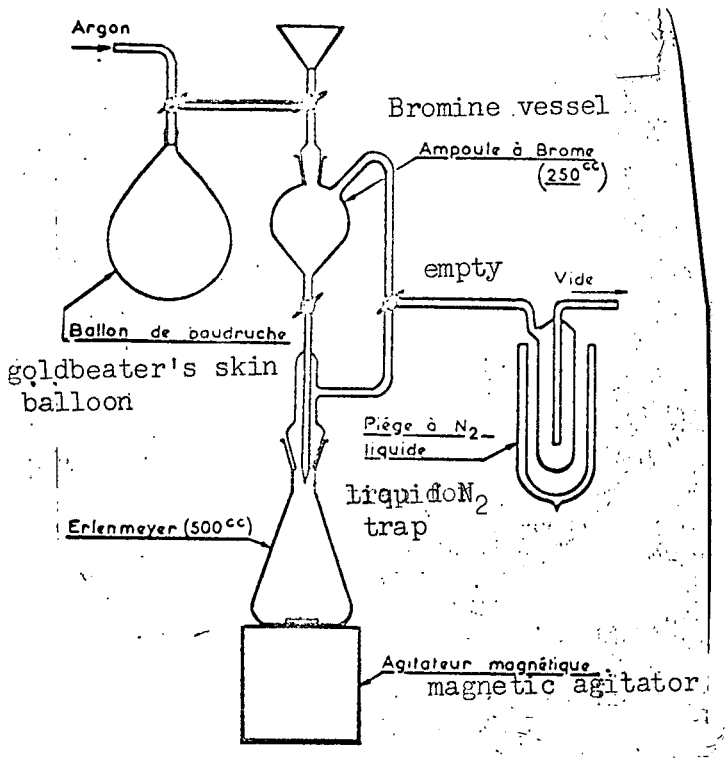


Fig.9. Apparatus for measuring the degree of oxidation of products of nickel nitrate decomposition.

DECOMPOSITION OF $Ni(NO_3)_2$, $6H_2O$ IN OPEN AIR

This study has been conducted in a manner completely identical to the preceding one: the results are presented in Tables VII and VIII and Figs 10 and 11.

PREPARATION OF $NiOOH_\gamma$

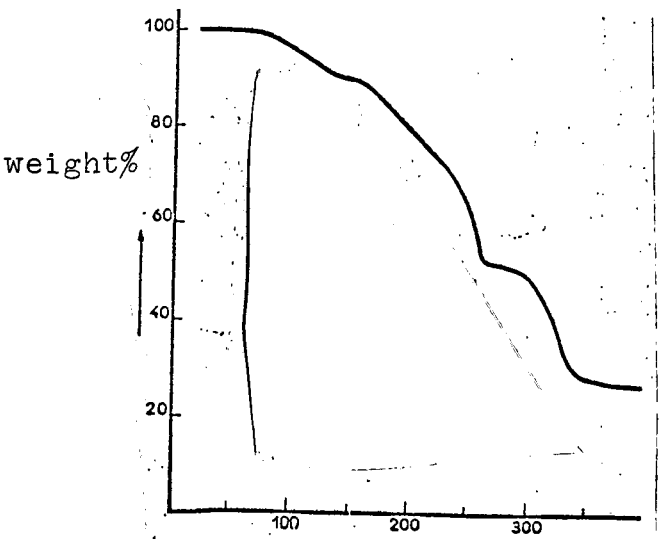
Glemser and Einerhand (Ref.10) have signalled the preparation of a hydroxide of trivalent nickel $NiOOH_\gamma$ by fusing a mixture of

E

Table V. Thermal Decomposition of $Ni(NO_3)_2$, $6H_2O$ in a vacuum

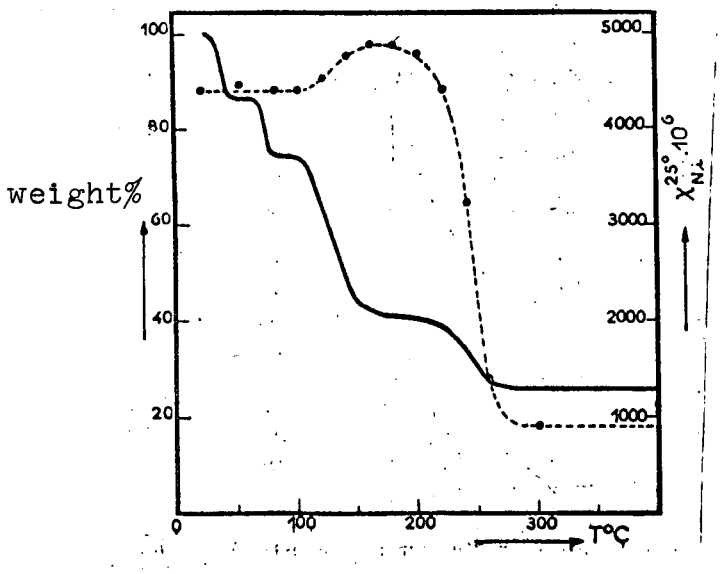
Sample	Sampling temp. (°C)	Formulas	X Spectra	$\chi^{25°}_{Ni} \cdot 10^6$ (*)
A	–	$Ni(NO_3)_2$, 6 H_2O	$Ni(NO_3)_2$, 6 H_2O	4 390
B	20	$Ni(NO_3)_2$, 4 H_2O	$Ni(NO_3)_2$, 4 H_2O + $\varepsilon Ni(NO_3)_2$, 6 H_2O	4 390
C	40	$Ni(NO_3)_2$, 2,25 H_2O	$Ni(NO_3)_2$, 4 H_2O + $Ni(NO_3)_2$, 2 H_2O	4 350
D	60	$Ni(NO_3)_2$, 2,1 H_2O	*Idem*	4 350
E	80	$Ni(NO_3)_2$, 2 H_2O	$Ni(NO_3)_2$, 2 H_2O	4 320
F	120	$Ni(NO_3)_2$, 1,5 H_2O	$Ni(NO_3)_2$, 2 H_2O + $Ni(NO_3)_2$	4 390
G	140	$Ni(NO_3)_2$, 0,1 H_2O	*Idem*	4 530
H	160	$Ni(NO_3)_2$	$Ni(NO_3)_2$	4 580
I	180	$Ni(NO_3)_2$	*Idem*	4 480 (4 580)
J	200	0,73 $Ni(NO_3)_2$ + 0,27 NiO	$Ni(NO_3)_2$ + NiO	3 520 (3 515)
K	220	0,28 $Ni(NO_3)_2$ + 0,72 NiO	*Idem*	1 820 (1 740)
L	240	0,07 $Ni(NO_3)_2$ + 0,93 NiO	*Idem*	1 015 (910)
M	260	0,05 $Ni(NO_3)_2$ + 0,95 NiO	NiO	965 (832)
N	300	$\varepsilon Ni(NO_3)_2$ + NiO	*Idem*	875
O	400	NiO	*Idem*	730

(*)The figures between parentheses represent the magnetic susceptibility calculated starting with the composition determined by chemical analysis.



Thermogravimmetry (150°/hour) of $Ni(NO_3)_2$, 6 H_2O in open air

Fig. 10



Thermogravimmetry (1o°/day) and magnetic susceptibility of $Ni(NO_3)_2$, 6 H_2O in open air

Fig.11

$NaOH + Na_2O_2$ in a nickel crucible and hydrolysis of the formed products. We have repeated this preparation method. The operation with the nickel crucible has been underway for about 24 hours. The product obtained in this manner was washed abundantly while carefully eliminating the flakes of $Ni(OH)_2$ formed in the course of hydrolysis. We have subsequently performed its chemical analysis, its X-ray spectrum and its magnetic investigation.

We have made an attempt to oxidize $Ni(OH)_2$ by the same mixture $NaOH + Na_2O_2$ in fusion. After hydrolysis and washing, chemical analysis, the X-ray spectrum and the magnetic investigation is demonstrated the presence of NiO and not of the superior oxide.

EXPLAINING THE RESULTS AND DISCUSSION

1. Decomposition of hexahydrated nickel nitrate.

a) Chemical and crystallographic investigations.

The thermal decomposition of $Ni(NO_3)_2$, $6H_2O$ leads to NiO passing through the intermediary stages $Ni(NO_3)_2$, $4H_2O$; $Ni(NO_3)_2$,$2H_2O$ and $Ni(NO_3)_2$, $2Ni(OH)_2$ in open air (Table VII and Fig. 11), as shown by chemical analysis and X-ray spectrum. These results confirm the recent investigation of Wiegel, Imelik and Lafitte (Ref.20) on the prolysis of $Ni(NO_3)_2$, $6H_2O$ in open air which have shown for the first time the presence of a basic salt in the decomposition of nitrate. It was possible to determine that the decomposition under a limited vacuum (10mm Hg) or in a flow of dry nitrogen causes the appearance -- as a preponderant phase -- $Ni(NO_3)_2$ with a weak proportion of the vapor of freed water during

Table VI. Thermal variation of the magnetic susceptibility of $Ni(NO_3)_2$, $6H_2O$ decomposition products in a vacuum

A		B		C		D		E		F		H	
T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$
77	15 990	77	16 210	77	15 890	77	16 170	77	14 990	77	15 190	77	15 750
98	12 390	101	11 910	103	11 480	102	11 730	103	11 060	103	11 170	101	11 860
119	10 430	122	10 060	123	9 750	123	9 700	125	9 360	124	9 570	125	9 810
151	8 410	145	8 620	142	8 400	143	8 540	145	8 170	145	8 310	144	8 530
183	7 030	164	7 750	160	7 550	163	7 580	164	7 330	165	7 250	165	7 620
213	6 020	184	6 850	180	6 830	183	6 870	184	6 650	185	6 650	187	6 820
252	5 120	222	5 770	213	5 840	219	5 770	223	5 590	226	5 620	226	5 900
293	4 460	257	5 050	216	5 730	254	5 110	259	4 920	258	4 970	261	5 170
		289	4 520	252	5 110	291	4 450	291	4 420	294	4 440	289	4 720
				293	4 425								

I		J		K		L		M		N		O	
T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$
77	16 580	77	12 560	77	5 645	77	1 977	77	1 519	77	1 051	77	750
105	11 730	103	9 150	104	4 170	108	1 747	108	1 322	108	987	108	708
127	9 810	127	7 560	126	3 510	135	1 591	138	1 242	136	951	135	689
148	8 370	147	6 540	147	3 035	161	1 426	162	1 190	160	940	161	689
164	7 550	168	5 800	165	2 775	189	1 304	190	1 127	193	937	191	691
186	6 880	190	5 290	188	2 520	226	1 156	230	1 052	229	908	228	697
226	5 740	231	4 400	230	2 180	270	1 042	278	977	273	887	273	713
259	5 070	270	3 920	294	1 825	296	1 014	294	964	296	876	297	730
294	4 540	292	3 570										

Formula: $NiO_{1.499}$, 1,15 H_2O $\chi_{Ni}^{25°} = 2\,060.10^{-6}$

T° K	77	103	124	147	173	201	204	240	290
$\chi_{Ni}^{corr}.10^6$	11 980	7 300	5 780	4 620	3 740	3 170	3 140	2 610	2 120

the first stage of dehydration.

Although we have established a low oxidizing capacity of the product of decomposition of $Ni(NO_3)_2$ and of $Ni(NO_3)_2$, $2Ni(OH)_2$, there is no possibility to prepare NiO_2 or even Ni_2O_3 by this method and it would seem reasonable to assume as LeBlanc and Sachse (Ref. 21), an absorption of oxygen on the NiO. This hypothesis is confirmed, in addition, by the fact that thermogravimetric curves and variation curves of magnetic susceptibility (Figs 8 and 11) do not offer any level which could correspond to a definite superior oxide.

b) Magnetic investigation at roome temperature.

At the start of the prolysis, be it in a vacuum or under open air (Tables V and VII, Figs. 8 and 11) the magnetic susceptibility $\chi_{Ni}^{25°}$ remains constant, with only the small eroors of measurement. $Ni(NO_3)_2$, $6H_2O$, $Ni(NO_3)_2$, $4H_2O$ and $Ni(NO_3)_2$, $2\ H_2O$ then possess the different magnetic susceptibilities due only to their different states of dehydration. On the other hand, we established a considerable increase in $\chi_{Ni}^{25°}$ in $Ni(NO_3)_2$ and especially in $Ni(NO_3)_2$, $2\ Ni(OH)_2$. This is not surprising in the case of the last compound as the susceptibility of Ni in $Ni(OH)_2$ is superior to that of nickel in nitrate of nickel.

$$(Ni(OH)_2 : \chi_{Ni}^{25°} = 4\,720.10^{-6},\ Ni(NO_3)_2 : \chi_{Ni}^{25°} = 4\,580.10^{-6}).$$

As soon as NiO appears, the susceptibility decreases rapidly while at the same time its contents increase, but is slightly

Table VII. Thermal decomposition of $Ni(NO_3)_2$, $6H_2O$ in air

Sample	Sampling Temp (°C)	Formulas	X Spectra	$\chi^{25°}_{Ni} \cdot 10^6$ (*)
A	—	$Ni(NO_3)_2$, 6 H_2O	$Ni(NO_3)_2$, 6 H_2O	4 390
B′	50	$Ni(NO_3)_2$, 4 H_2O	$Ni(NO_3)_2$, 4 H_2O + $Ni(NO_3)_2$, 6 H_2O	4 450
C′	80	$Ni(NO_3)_2$, 2,1 H_2O	$Ni(NO_3)_2$, 4 H_2O + $Ni(NO_3)_2$, 2 H_2O	4 410
D′	100	$Ni(NO_3)_2$, 2 H_2O	$Ni(NO_3)_2$, 2 H_2O	4 390
E′	120	0,62 [$Ni(NO_3)_2$, 2 H_2O] + 0,13 [$Ni(NO_3)_2$, 2 $Ni(OH)_2$]	$Ni(NO_3)_2$, 2 H_2O + $Ni(NO_3)_2$, 2 $Ni(OH)_2$	4 520
F′	140	0,21 [$Ni(NO_3)_2$, 2 H_2O] + 0,26 [$Ni(NO_3)_2$, 2 $Ni(OH)_2$]	*Idem*	4 750
G′	160	1/3 [$Ni(NO_3)_2$, 2 $Ni(OH)_2$]	$Ni(NO_3)_2$, 2 $Ni(OH)_2$	4 870
H′	180	1/3 [$Ni(NO_3)_2$, 2 $Ni(OH)_2$]	*Idem*	4 880
I′	200	0,31 [$Ni(NO_3)_2$, 2 $Ni(OH)_2$] + 0,06 NiO	$Ni(NO_3)_2$, 2 $Ni(OH)_2$ + NiO	4 780 (4 575)
J′	220	0,28 [$Ni(NO_3)_2$, 2 $Ni(OH)_2$] + 0,14 NiO	*Idem*	4 410 (4 190)
K′	240	0,18 [$Ni(NO_3)_2$, 2 $Ni(OH)_2$] + 0,46 NiO	*Idem*	3 220 (2 930)
L′	260	0,05 [$Ni(NO_3)_2$, 2 $Ni(OH)_2$] + 0,86 NiO	*Idem*	1 395 (1 280)
M′	300	ε[$Ni(NO_3)_2$, 2 $Ni(OH)_2$] + NiO	NiO	905
N′	400	NiO	NiO	895

(*) Figures in parentheses represent the magnetic susceptibilities calculated starting with the compound determined by chemical analysis.

Table VIII. Thermal variation of the susceptibility of the decomposition products of $Ni(NO_3)_2$ in the air.

A		C'		D'		E'		F'		G'		H'	
T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$
77	15 990	77	16 290	77	15 650	77	18 350	77	18 910	77	24 920	77	24 790
98	12 390	102	11 870	101	11 560	105	12 450	103	14 300	102	16 500	101	16 290
119	10 430	127	9 720	128	9 560	126	10 430	124	11 750	127	12 760	124	12 970
151	8 410	150	8 260	148	8 380	148	8 740	145	9 970	149	10 450	125	12 680
183	7 030	171	7 360	166	7 440	189	6 950	169	8 490	169	9 080	146	10 580
213	6 020	186	6 750	188	6 570	229	5 770	189	7 520	194	7 800	169	9 030
252	5 120	220	5 790	227	5 570	264	5 100	225	6 330	235	6 300	193	7 850
293	4 460	250	5 200	264	4 980	296	4 555	262	5 340	267	5 440	230	6 380
		293	4 470	294	4 440			294	4 800	297	4 890	264	5 590
												298	4 885

I'		J'		K'		L'		M'		N'	
T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$	T° K	$\chi_{Ni}^{corr}.10^6$
77	24 920	77	21 420	77	13 960	77	2 985	77	1 069	77	1 040
100	16 950	103	14 480	100	9 730	109	2 230	118	935	106	941
130	12 220	105	14 040	129	7 280	139	1 940	135	922	135	914
157	9 790	130	10 960	158	5 870	160	1 775	158	912	162	905
189	7 780	150	9 240	186	4 980	194	1 645	186	908	190	902
225	6 520	180	7 580	225	4 170	235	1 510	224	902	227	899
263	5 550	215	6 160	263	3 610	280	1 430	276	902	270	905
294	4 840	251	5 390	296	3 240	294	1 390	296	905	295	896
		292	4 490								

superior (Tables V and VII) to the susceptibility calculated starting with the composition determined by the chemical analysis accepting respectively for $Ni(NO_3)_2$, $Ni(NO_3)_2$, $2Ni(OH)_2$ and NiO the values $\chi_{Ni}^{25°}$ = 4,580 · 10^{-6}, 4880· 10^{-6} and 635 · 10^{-6} (Ref.22) measured experimentally. This divergence must be attributed to the presence of a small amount of absorbed paramagnetic gas (O_2 and NO_2) originating from the decomposition of the nitrate. This hypothesis finds its justification in the fact that we have detected a low oxidizing capacity of the samples considered and that the divergence is larger for prolysis performed in open air than for that performed in a vacuum.

c) Magnetic investigation depending upon temperature.

The thermomagnetic investigation (Tables VI and VIII) makes possible to draw curves of $1/\chi = f(T)$ (Fig.12). The points relating to $Ni(NO_3)_2$, $6H_2O$, $Ni(NO_3)_2$, $4H_2O$, $Ni(NO_3)_2$, $2H_2O$ and $Ni(NO_3)_2$, $2Ni(OH)_2$ are well aligned and we can calculate effective magnetic moments and the Curie temperatures of the following compounds:

$Ni(NO_3)_2$, 6 H_2O / $Ni(NO_3)_2$, 4 H_2O	$p_{eff} = 3{,}26\ \mu_B$	$\theta = -10°K$(*)
$Ni(NO_3)_2$, 4 H_2O	$p_{eff} = 3{,}32\ \mu_B$	$\theta = -20°K$
$Ni(NO_3)_2$, 2 $Ni(OH)_2$	$p_{eff} = 3{,}29\ \mu_B$	$\theta = 21°K$

These results indicate a slight variation of θ while the p_{eff} is remarkably constant and approximately equal to the magnetic moment of $Ni(OH)_2$ ($p_{eff} = 3.26\ \mu_B$, $\theta = 21^oK$) and other nickel

*)This value is in good agreement with the result obtained by Janes (Ref.23): $p_{eff} = 3{,}24\ \mu_B$, $\theta = -7°$ K.

salts with a relatively strong orbital contribution.

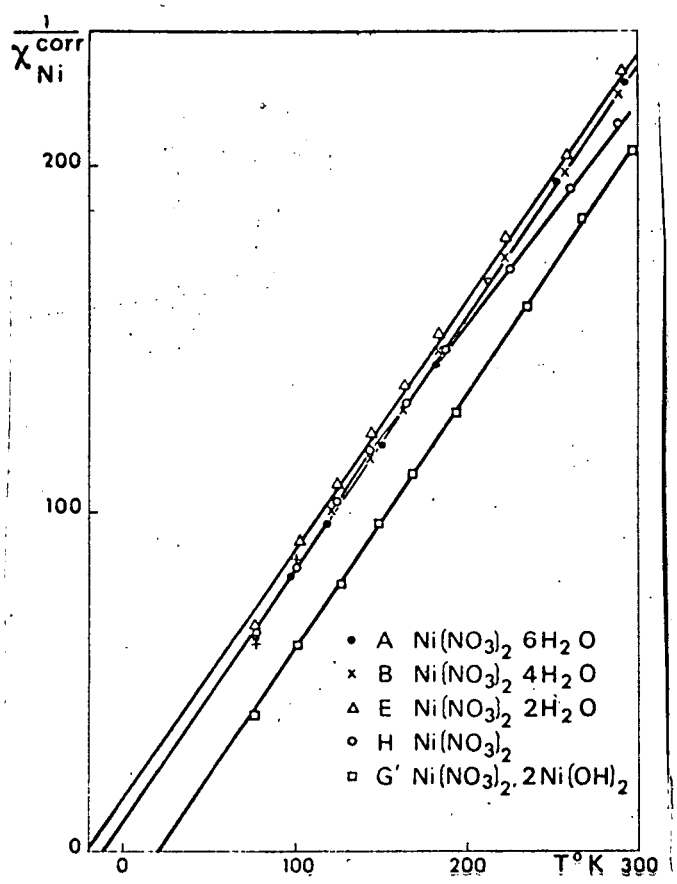


Fig. 12. Thermomagnetic Study of Nickel Nitrate

In the case of $Ni(NO_3)_2$ we establish a slight curvature of the straight $1/\chi = f(T)$. This phenomenon found in many compounds of nickel has already been made the subject of a discussion in the preceding article on superior hydroxides. It is possible to approximately break down the thermomagnetic variation of the nitrate of anhydrous nickel into two sections:

between 77 and 150°K $p_{eff} = 3,21\ \mu_B$ $\theta = -4°K$
between 150 and 300°K $p_{eff} = 3,50\ \mu_B$ $\theta = -34°K$

As the antiferromagnetic NiO appears, the $1/\chi$ variation depending upon the temperature diminishes and ceases to be linear. The measured susceptibilities are still at this point systematically superior to the calculated susceptibility starting with the compound determined by the analysis, considerable divergences may appear at 77°K. This is explained easily, if we notice that Ni^{++} (in $Ni(NO_3)_2$) and in $Ni(NO_3)_2$, $2Ni(OH)_2$) have at 77°K a susceptibility approximately thirty times higher than NiO (Ref.22). In this case no comparison is possible any more as the slightest error in the analytical determination of $Ni(NO_3)_2$ or of $Ni(NO_3)_2$, $2Ni(OH)_2$ leads to a considerable error in the calculated susceptibility. We shall state here only that samples O and N' have susceptibilities superior to those of pure NiO and their thermomagnetic behavior does not conform to that of NiO (Ref.24). Heating to 400°C is therefore insufficient for the preparation of pure NiO as it still retains either a small amount of nitrate or the absorbed gases. Determining the state of complete purity is at this point much more precise by the magnetic method than by the chemical analysis method.

2. Nickel Oxidation by Means of Sodium Peroxide.

Chemical and crystallographic analyses reveal the anticipated formation of hydroxide $NiOOH_Y$. For this compound of trivalent

nickel we have established by means of the curve $1/\chi = f(T)$ (Fig.13)

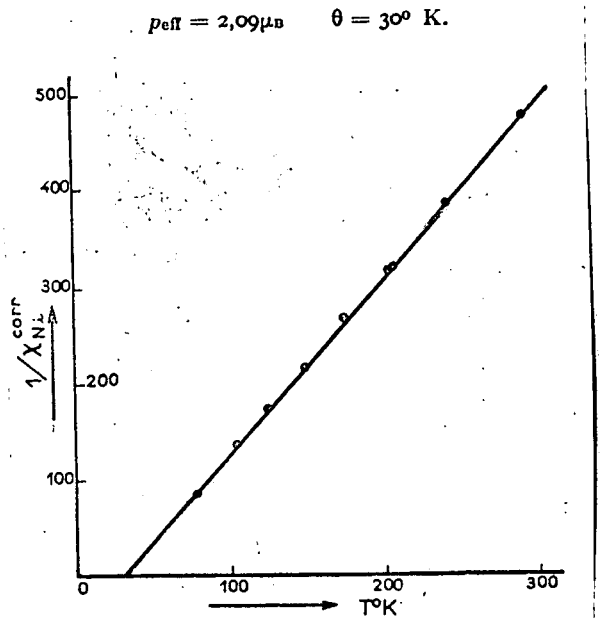


Fig. 13. Thermomagnetic investigation of γ-NiOOH.

The effective magnetic moment is superior to the theoretical value of the spin moment (1.73 μ_B) in a compound possessing only one non-paired electron. The contribution of the orbital moment to the experimental magnetic moment is not negligible and is comparable to that established for $Ni(OH)_2$.

This result should be tied in with the result already obtained for NiOOHβ, whose magnetic moment equally corresponds to one single unpaired electron, while the free ion Ni^{+++} possesses 3 such electrons. This phenomenon -- also found in the organic compounds

of Ni^{+++} seems thus to be general and should be attributed to the fact that the energy of the crystalline field is superior to that of the electron pairing, which consequently produces a correlative decrease in the observed magnetic moment. In the same manner we may explain the reason why the compounds of Ni^{4+} have a magnetic moment corresponding to 0 electron which is unpaired while the free ion Ni^{4+} contains 4 of them.

THIRD PART

MAGNETOCHEMICAL INVESTIGATION OF ELECTROCHEMICAL TRANSFORMATIONS OF NICKEL HYDROXIDE IN AN ALKALINE MEDIUM

The investigation of the electrochemical behavior of superior nickel hydroxides in a base medium is of great interest from the theoretical point of view as well as from the practical one, since the creation of alkaline accumulators. Thus it is not surprising that we may state that for more than half a century, numerous authors have been particularly interested in this subject (Ref.1). Despite the progress acheived due to the recent works of Briggs (Ref.25) and his collaborators, Glemser and Einerhand (Ref.26) and Falk (Ref.27), certain divergences and contradictions still persist. The magnetic investigation of the evolution of nickel hydroxides during polarization in an alkaline medium compared to a magnetochemical investigation would seem to be interesting and could possibly provide a considerable contribution for a better understanding of the charge-discharge mechanism of the positive elect-

rode of nickel hydroxide.

Research in $Ni(OH)_2$ Mixed With Graphite

1. Elaboration of one polarization cell.

In the industrial production process of alkaline accumulators of the $Ni(OH)_2$ -- not being a conductor-- is generally mixed with graphite or to nickel in flakes. Yet these electrodes are not convenient for a quantitative work for numerous reasons. Particularly, the amount of active material present in the electrode is not precisely known, and neither is the nature of the impurities which may be retained by the electrode. In addition, the presence of ferromagnetic nickel playing a supporting part or that of the electrode coating cannot be tolerated in a magnetic research. Therefore, we have used plexiglass cells: a material which resists concentrated potassium solutions which are weakly dimagnetic. The support of the electrode of nickel hydroxide is achieved by agglomerated graphite or platinum sheet. The counter-electrode is also made of platinum. The cells contain the reference electrode Hg/HgO in contact with the electrolytic solution.

We have been led to develop several types of cells aiming for perfection, until the tests effevted on the active industrial material ($Ni(OH)_2$ = 80%, graphite: 20%) brought full satisfaction. We have retained only three of those (Fig.14) which have been most used. Cell 1 which has served during the tests is essentially composed of the cylindrical cell C itself which in turn contains the support of the electrode S in graphite. A clamping

F

screw V, perforated and made of plexiglass holds the pellet P made of active material ($Ni(OH)_2$ + graphite) against the support S. The counter-electrode E of platinum is placed at the top. We were able to determine that the contact between the granules of the active material and that of the active material with the electrode support is improved when the pellets are used. Graphite electrode support also contributes to the improvement as compared to platinum use. However, the yield established, starting with the duration of the first level discharge does not exceed 30% of the theoretical value calculated, starting with the $Ni^{3+} \rightarrow Ni^{2+}$ transformation. This value is too weak and it is due, in all probability, to the fact that a major part of the active material is found in the cell outside the current lines, and a certain amount may even not be attained by the electrolyte.

In order to increase the surface of the contact between the electrolyte and the active material we have placed, at the separation point of these two phases a sintered glass F which is supported by means of a clamping ring B made of plexiglass (Fig. 14, cells II and III). A reference electrode R Hg/HgO is equally added to the device to make possible the measurements of the potential. Finally, in order to preclude the discharge important to the counter-electrode from provoking electrolyte projections outside, we have adapted, for each cell, a cover equipped with a washer, both pierced by a hole located in such a manner as to avoid external projections, while permitting the gaseous discharge. A complete airtightness of the cell has been obtained by gluing the reference electrode and the electrode support by means of Col-

loplex. All results presented below are due to the use of calls I and II.

2. Mounting the Cell on a Magnetic Balance.

In order to reduce to a minimum manipulations which always may generate errors, we have placed the cell connected with the polarization circuit in the "measuring" position on the magnetic balance. Upon trying various devices, the problem consisting in the bringing of the lead conductors with connection forces practically equal to zero, or easily measured, to the cell, has been resolved by using a silver band without torsion of very small width and especially, thickness, which, placed horizontally between the cell and a point of support on the exterior did not cause any measurable perturbation when the height of the cell varied several millimeters.

The diagram presenting the mounting of the cell onto the magnetic balance of Gouy-Pascal is presented in Fig. 15. The cell C to which we have adapted a glass loop is suspended on a nylon thread affixed to the precision balance B by means of a glass cross V. At the ends and at the center of the horizontal stem, platinum threads are wound in a, b, c at respective ends a_1 and a_2, b_1 and b_2, and c_1 and c_2. The three platinum threads coming from the electrode of nickel oxide, from the platinum counter-electrode and from the reference electrode are welded in points a_1, b_1 and c_1. In order to keep the assembly rigid, the windings a, b and c which would have a tendency to wind around

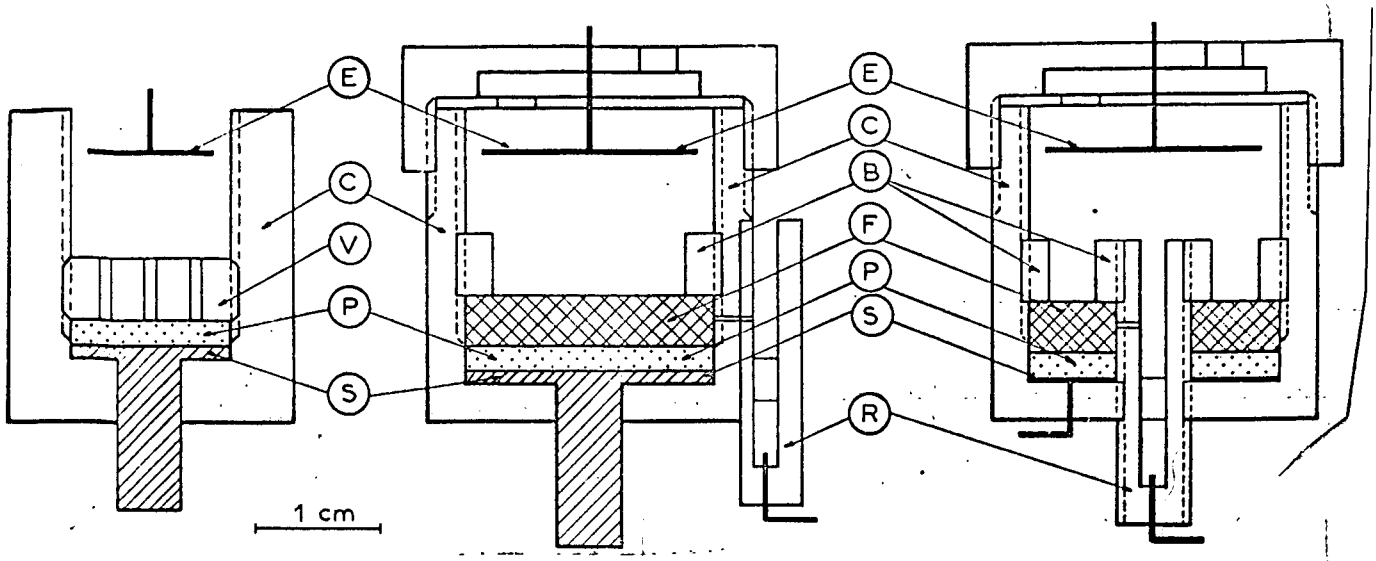


Fig. 14. Polarization cells

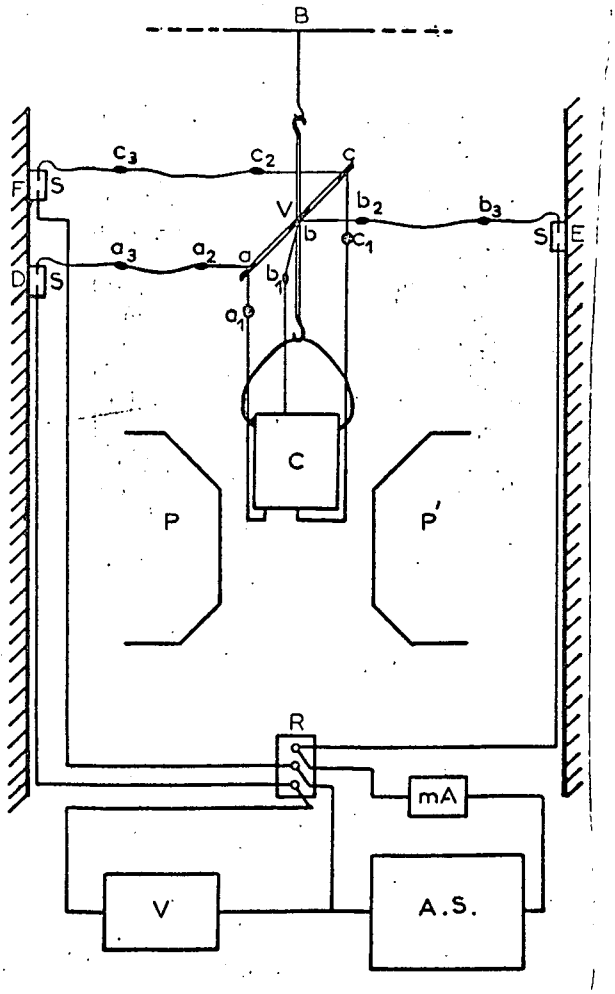


Fig. 15. Mounting the cell on the magnetic balance

the stem in glass are glued to the latter with araldite. Three clamps S are affixed to the sides of the balance cage of Pascal at points D, E and F at the same height as a_2, b_2 and c_2. They hold the three rigid threads at the a_3, b_3 and c_3 points. Between a_2 and a_3, b_2 and b_3 and c_2 and c_3 we weld, at each end three threads a_2a_3, b_2b_3 and c_2c_3 of the silver band without torsion (width: 15%mm). Finally, we establish contact with the three relay terminals R by means of a copper thread. It will then be possible to close the circuit of the current generator and the measuring devices. The assembly consisting of cell C -- glass cross V -- precision balance B can be displaced vertically in a magnetic field which exists between the pole parts P and P' of the electromagnet by means of a jack operated by an electric motor. The cell C is suspended by means of a nylon thread to the precision balance platform (1/10mg). The polarization circuit consists of a stabilized feeding either by current or by potential of the SOLEA type, ASC 3C and a milliampermeter. The potential of the nickel oxide electrode is measured in relation to the reference electrode by means of a potentiometer A.O.I.P. or is directly recorded on a recording galvanometer of the S.E.F.R.A.M. type, Graphispot, type G.R.V.A.C. with an impedance at the start of 4 M Ω/V.

3. Preliminary Results.

Our first measurements have been made with a mixture of $Ni(OH)_2$ plus graphite of industrial make by means of the cell I (Fig. 14).

The latter placed in the air gap is displaced vertically in the magnetic field and we have measured, for each position, the magnetic force F and the height of the cell reported to a fixed mark by means of a cathetometer, (Fig. 16).

Charging the cell of polarization for 20 hours with a current in milliamperes corresponding 1/10 of the theoretical capacity expressed in milliamperes and calculated starting with the $Ni^{2+} \rightarrow Ni^{3+}$ transformation results in a considerable decrease in the paramagnteism of $Ni(OH)_2$. On the other hand, the former is the larger, the greater the capacity taken by the electrode. We notice also that when the number of cycled of the charge-discharge increases, the electrode capacity grows to a limit value. We then say that the active material has been "formed".

The curves (5), (7) and (9) relating to the discharged active material show an increase in paramagnetism, which, however, does not attain its initial value. This fact would seem to indicate that the discharged cell still contains nickel in a state of valence exceeding 2, which agrees with the deductions of Briggs and his co-workers (Ref.25) who found non-negligible amounts of active oxygen in completely discharged electrodes.

Before drawing any conclusions as to the nickel hydroxide it is necessary to investigate to perfection the part played by the graphite in the electrode. For this reason we have once more taken up the preceding experiences with the graphite electrode (pellets consisting of nuclear graphite lamella). We have then obtained the lattice of curves presented in Fig. 17. We can then

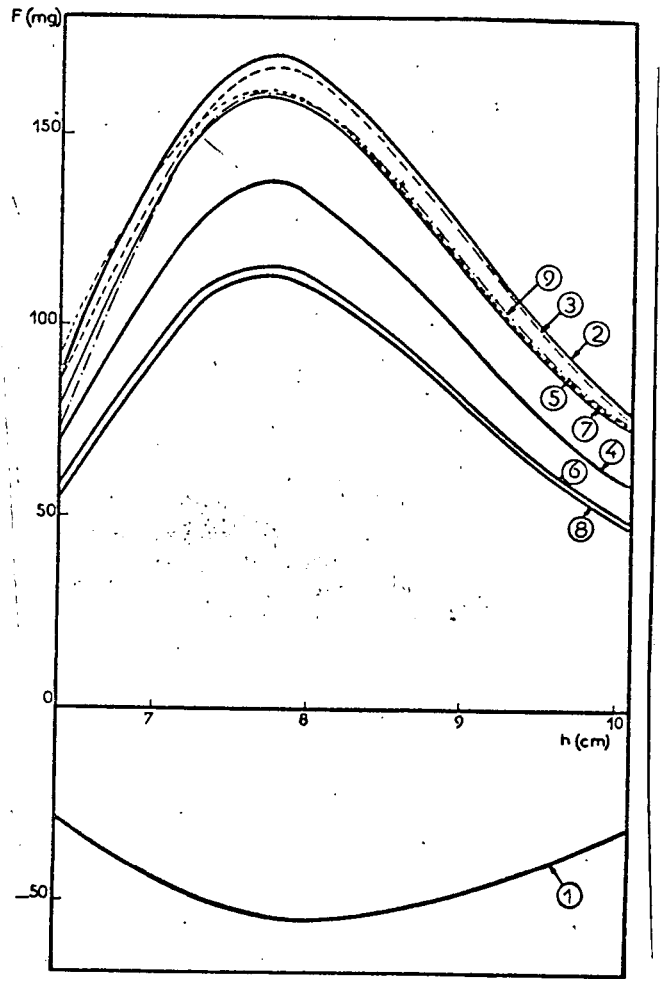


FIG. 16.

1) Empty cell (14.001gr)

2) Cell + pellet of $Ni(OH)_2$ and graphite (1.036gr)

3) Cell + pellet + KOH-SN (0.470gr)

4) Cell charged for 24 hours at 24 mA

5) Discharged Cell (capacity corresponding to the 1st discharge level = 38 mAh)

6) Rechrged cell 20 hours at 24 mA

7) Discharged cell (cap. corresponding to 1st discharge level = 62mAh)

8) Recharged cell 20 hours at 24mA

9) Discharged cell (cap. corresp. to 1st dischage level =67mAh)

state that if the charge does not seem to affect to any considerable degree the extent of magnetism in the graphite, the discharge, on the contrary, results in a non-reversible decrease in its diamagnetism. However, the amount of graphiteconsidered at this point being very superior to that contained in an electrode composed of $Ni(OH)_2$ mixed with graphite (Fig.16), the magnetic variations caused by graphite during the charge and the discharge of a pellet of active material are very weak (2 to 3% approximately of the total fluctuation of magnetic force) and can therefore be disregarded in the first approximation.

4. Quantitative analysis.

In order to be able to effect a quantitative magnetic investigation it is indispensable to operate with completely pure products. $Ni(OH)_2$ has been prepared by the Teichner method (Ref.28) and we have crushed in a boron carbide mortar some nuclear graphite, keeping only the granules passing through the 25μ mesh.

It was subsequently necessary to mix thoroughly the two components in order to obtain a sufficient capacity for the charge. To this end we have used an agate and a boron carbide mortar and in spite of crushing and mashing during a several hour period we did not achieve good results. We have also tried, without success, the crusher consisting of a container equipped with a boron carbide lining on the inside, and in which a boron carbide knife revolved with varying speed -- capable of achieving 12,000 rpm. The only procedure to give us satisfaction was the crushing of the

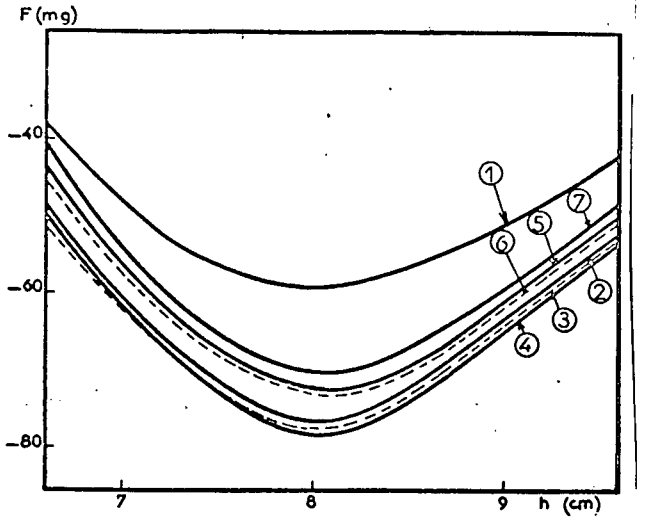


FIG. 17.

1) Empty cell

2) Cell and graphite pellet

3) Cell + pellet + KOH-5N

4) Cell charged 20 hours at 25 mA

5) Discharged cell 20 hrs at 25 mA

6) Recharged cell 20 hrs at 25mA

7) Discharged cell 20 hrs at 25 mA

mixture by means of a micro-crusher of the Dangomau type: namely, a tungsten carbide container containing the product to be crushed with ball bearings also of tungsten carbide, moving back and forth very rapidly (700 per min).

In order to still further improve the contact between nickel hydroxide and graphite we have prepared directly a mixture by adding the calculated amount of graphite powder (< 25μ) to the ammonia solution of nickel nitrate. The strongly agitated and

heated solution precipitates $Ni(OH)_2$ by coating the granules of graphite present in the solution. This powder in which $Ni(OH)_2$ and graphite are in close contact had, however, to be subjected to crushing in a container of tungsten carbide in order to make it a conductor. This last procedure gave us the active material which, offering the best efficiency was at last chosen to be used in our further studies. The mixture prepared in this manner contains 79.5% $Ni(OH)_2$ (Ni = $8.58 \cdot 10^{-3}$ atm g/g) and its specific magnetic susceptibility at 25°C is:

$$\chi^{25} = 39{,}3 \cdot 10^{-6}.$$

It was subjected to three cycles of charge-discharge by means of cell II (Fig. 14). The magnetic measurements have been effected during polarization and the electrode potential has been recorded at the moment of measurement. In order to achieve this, the cell has been kept fixed in the air gap at the most favorable height; in other words, where the measured force is at its maximum. When the corrections due to the empty container and to the electrolyte are determined in advance, it is possible to calculate the magnetic force to which only the active material pellet is subjected and, subsequently, to measure magnetic susceptibility (χ_1) of the latter.

If χ_1 and χ''_1 (*) are, respectively, median specific susceptibilities of the nickel hydroxide and of graphite, and x is the mass fraction of $Ni(OH)_2$ in the active material we have the following relation:

(*) see footnote next page

$$x\chi + (1 - x)\chi'' = \chi'$$

wherefrom:

$$\chi = \frac{\chi' - (1 - x)\chi''}{x}$$

and the susceptibility χ_{Ni} of the atom-gram of nickel equals:

$$\chi_{Ni} = [\chi' - (1 - x)\chi''] \frac{M}{x}$$

M being the molecular mass of nickel hydroxide and x/M the nickel content expressed in atm g/g of the mixture (= $8.58 \cdot 10^{-3}$).

We obtain finally (*)

$$\chi_{Ni} = \frac{\chi' + 1{,}34.10^{-6}}{8{,}58.10^{-3}}.$$

The χ_{Ni} susceptibilities of nickel hydroxide during positive and negative polarization established by means of this formula have subsequently been corrected of diamagnetism and returned to 25°C. The $\chi_{Ni}^{25°}$ values thus obtained are carried, depending upon the time of charge and discharge onto Fig. 18, which also carries the fluctuations of the electrode potential. As before, we have used such a polarization current as to have reaction $Ni^{2+} \rightleftharpoons Ni^{3+}$ theoretically attained in 10 hours. In addition, prior to each discharge the charged electrode was given a 1 hour rest. In the same manner we have achieved the other series of five cycles of charge-discharge, using the same active material. The results are presented in Fig. 19.

(*) χ' = - 6.7 . 10^{-6}. Although the graphite is strongly anisotropic, we can use this median value due to the very small dimensions of graphite granules, to the small amount of graphite in the active material and, most of all, because an error in the term $(1-x)\chi'$ has a relatively small influence upon the final result.

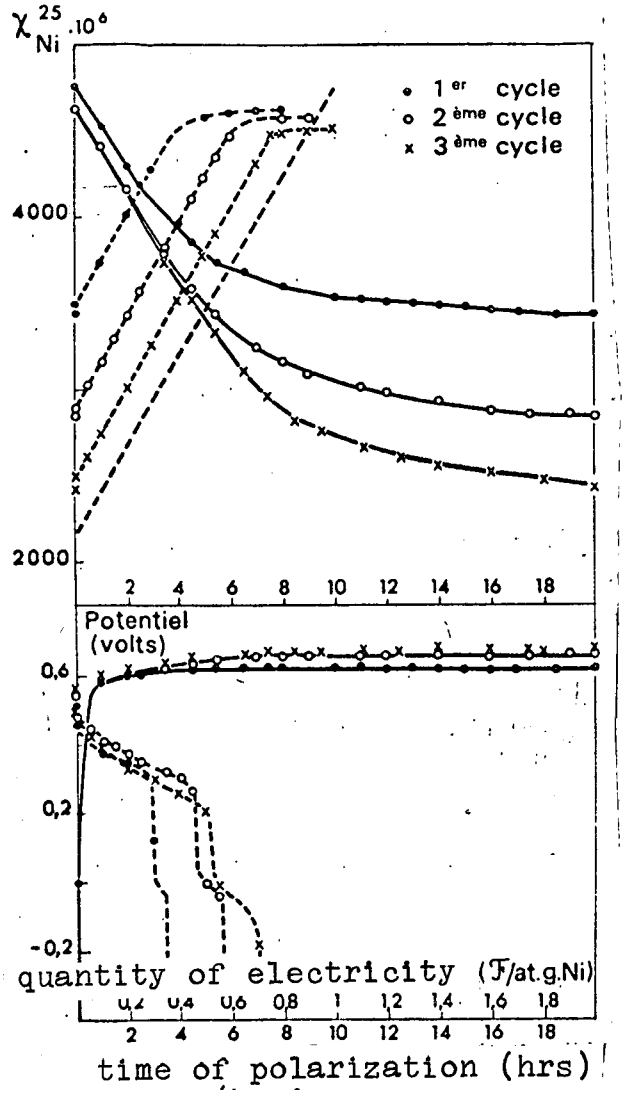


Fig. 18 Relation between the magnetic susceptibility, the potential and the polarization time of nickel hydroxide electrode

——— charge
---------- discharge

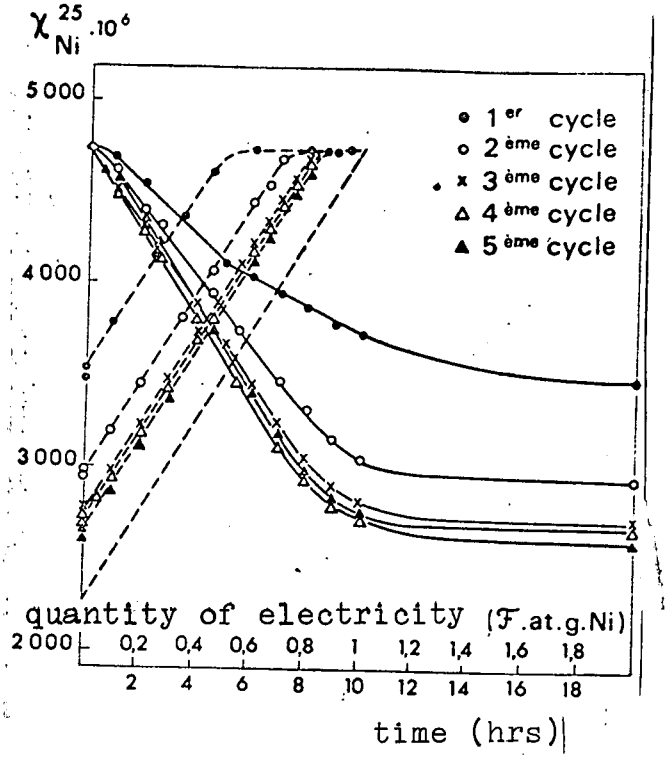


Fig. 19. Relation between the magnetic susceptibility and the polarization time of a nickel hydroxide electrode

——— charge
---------- discharge

5. Explaining the Results and Discussion.

During the charging, the decrease of $\chi_{Ni}^{25°}$ is rapid at first, and becomes later on gradually slower. The number of M^{++} ions transformed into Ni^{+++} ions during a given time and consequently the efficiency of the charge diminish when the duration of the ch charge increases. During the discharge, quite to the contrary, the magnetic susceptibility of nickel hydroxide increases in proportion with the polarization time until the electrode is completely discharged. These variations are the more considerable, the more the number of cycles increases. According to our first results this would reveal an increase in the capacity of the electrode to a certain limit achieved in the fourth cycle of the charge-discharge (Fig.19).

It is interesting to note the remarkable parallelism of curves relative to magnetic variations of the nickel hydroxide during the discharge. As the discharge current has been selected to have the Ni(III) nickel transformation into Ni(II) effected in exactly 10 hours, the tracing of a straight parallel to the preceding curves and passing through the initial value of the susceptibility of nickel hydroxide for a 10 hour period of time (Figs 18 and 19) gives to the time t = 0 the susceptibility of Ni(III), or, more precisely, the susceptibility of nickel hydroxide with a valence equal to 3 in median value, as the states of valence 2,3,4 may be simultaneously engaged in the charged active material. We establish then the following values:

$\chi_{Ni}^{25°} = 2\,150.10^{-6}$ (Fig. 18)
$\chi_{25}^{Ni} = 2\,240.10^{-6}$ (fig. 19).

By adopting themedian value $\chi_{Ni}^{25°} = 2200.10^{-6}$, we state that the latter is quite superior to the value $\chi = 1320 \cdot 10^{-6}$ established for NiOOHβ which would reveal the presence of Ni(II), Ni(III) and Ni(IV) whose respective atomic parts may be calculated (See 1st Part):

$$a = c = 0.423 \qquad b = 0.154$$

The curves in Fig. 18 represent the variations in the potential of the electrode (*) depending upon the time of polarization have been conforming to those which are generally obtained for electrodes of nickel hydroxide in alkaline accumulators (Ref.1). The presence of a second discharge level at approximately 0 V has been explained by the reduction in the oxygen absorbed either by graphite (Ref. 29) or by the hydroxide (Ref.27). In this case, the magnetic susceptibility should decrease. Yet, no anomaly appears on the curves which represent the magnetic variations which depend on the discharge time, the same straight line covering the entire discharge

(*) these potentials have been recorded in the presence of the polarization current as, during rest we would have had to wait to obtain equilibrium,for several hours. During this period, the electrode would have changed considerably. These potentials themselves are of little interest and we consider only the general behavior of their variations.

charge. This hypothesis must then be eliminated and we should, on the contrary, admit that the reduction in the superior nickel hydroxide is continued until the start of the hydrogen discharge (at approximately 1 V).

Research on $Ni(OH)_2$ Impregnated in Sintered Platinum Electrodes.

1. Method of Operation.

From the point of view of industry, the electrodes containing graphite and nickel flakes traditionally used to give the active material conductivity reveal more and more the tendency to be replaced by electrodes of sintered nickel and impregnated with $Ni(OH)_2$. Here again, the presence of ferromagnetic nickel which we could not use in our study forced us to use sintered platinum (with a diameter of 2cm and a thickness of 2 to 3 mm) resting on a platinum sheet (with a 2 cm diameter and a 0.5mm thickness) and a platinum thread welded onto its center. The pores have very small dimensions (several μ) and the porosity os of approximately 60%.

After impregnation in the vacuum by means of $Ni(NO_3)_2$, $6H_2O$ at 50°C, $Ni(OH)_2$ is precipitated by means of NaOH - 5N at 80°C during 4 hours. The electrode is subsequently washed in water at 80°C during 4 hours, finally driedin an oven during 15 hours at 110°C. The polarization of the electrode in an alkaline medium (KOH - 5N) has been achieved in a C cell made of glass and comprising and R alaectrode of reference Hg/HgO and a counter-electrode E in platinum (Fig. 20). Immediately after having

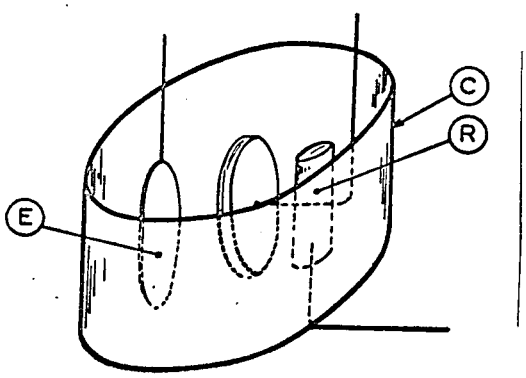


Fig. 20. Polarization cell.

charged the electrode for a given time (30 min., 1 hour....up to 16 hours) using a current of a strength which would allow the reaction Ni(II) $\longrightarrow$ Ni(III) to set in theoretically in 4 hours, we have determined the potential, the magnetic susceptibility and the oxidation degree of the nickel hydroxide. Chemical analysis has been performed, keeping, for a 4 hour period in an inert atmosphere (nitrogen R) the electrode in an agitated solution of SO_4H_2 - 4N (50 cu cm) in the presence of KI. After a partial neutralization by means of 150 cm^3 of NaOH $\frac{n}{2}$ N, the amount of freed iodine and the nickel content have been approtioned respectively, by a hyposulfite solution N/50 and by cyanometry (Ref.5). We have also made measurements during the discharge. The electrode had been charged for 16 hours before the discharge.

2. Results.

The results are grouped in Table IX and Figs. 21 and 22 (p.60).

3. Explaining the Results and Discussion.

We notice from the start that these electrodes are far more

Table IX. Properties of sintered platinum electrodes impregnated with $Ni(OH)_2$ during polarization

	polarization time (hrs)	O_{active}/Ni	$\chi^{25°}_{Ni} \cdot 10^6$	Potential (V)
Charge	0	0	4 750	
	1/2	0,060	4 400	0,525
	1	0,128	4 080	0,540
	1 1/2	0,1875	3 800	0,535
	2	0,268	3 450	0,545
	2 1/2	0,319	3 130	0,550
	3	0,393	2 660	0,560
	3 1/2	0,470	2 270	0,550
	4	0,526	2 120	0,550
	5	0,595	1 600	0,600
	6	0,700	1 300	0,610
	8	0,736	1 120	0,605
	12	0,755	1 010	0,605
	16	0,775	840	0,595
Discharge	1	0,626	1 440	0,400
	1 1/2	0,575	1 620	0,375
	2	0,510	2 000	0,380
	2 1/2	0,500	2 060	0,365
	3	0,416	2 530	0,355
	4	0,280	3 300	0,350
	4 1/2	0,252	3 260	— 0,220 (a)
	5	0,168	3 800	0,110 (b)
	6	0,06	4 380	— 1
	8	0,061	4 350	— 1 approx.

(a) end of second discharge
(b) start of second level

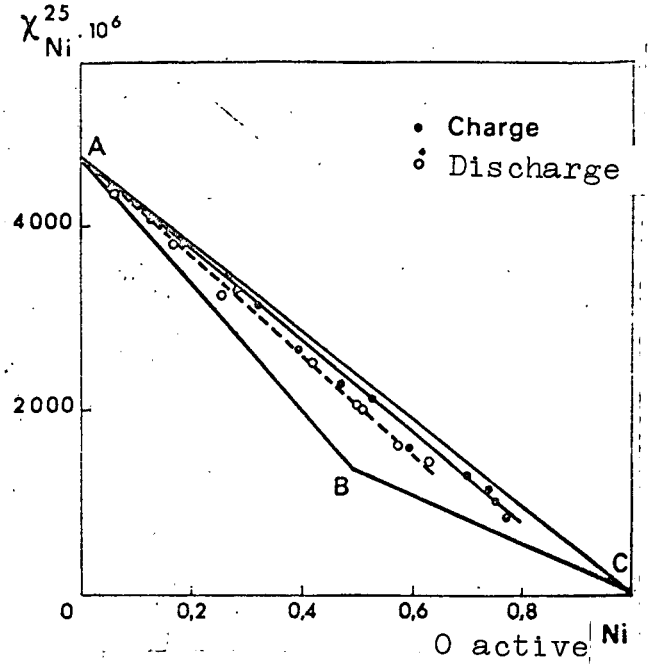


Fig. 21. Relation between magnetic susceptibility and oxidation degree of nickel hydroxide electrodes during polarization.

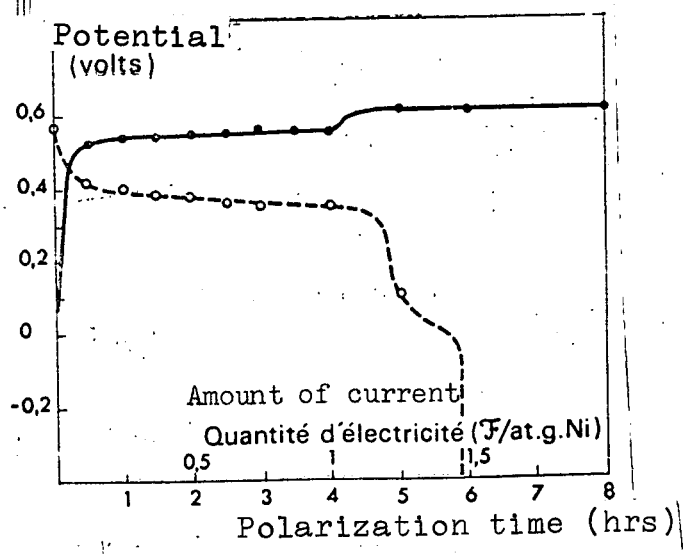


Fig.22.

Relation between the potential & polarization time of nickel hydroxide electrodes

satisfying than those containing graphite. For a similar amount of nickel hydroxide the capacity evidenced by the duration of the discharge to a high potential (Fig.22) is, in fact clearly superior here. On the other hand, the relation O_{act}/Ni whose measuring was made possible by using these sintered electrodes reaches the maximal value of 0.775. The nickel is found then in a state of oxidation largely superior to that which corresponds to nickel hydroxide (III) NiOOHβ. We have effectively checked by X-ray diffraction the fact that the hydroxide which was formed was actually NiOOHβ and not NiOOHγ. This operation is indispensable to provide a correct interpretation of the magnetic results, as the two preceding nickel (III) hydroxides do not possess the same magnetic susceptibility.

The magnetochemical study of the charge of $Ni(OH)_2$ (Fig.21) reveals the appearance of very close experimental points on the AC side of the ABC triangle identical with that represented in Fig. 2. We can then assume that $Ni(OH)_2$ is oxidized simultanously to a small extent in Ni (III) and to a major part in Ni (IV). It seems, however, more satisfying to admit that electrochemical oxidation leads first to Ni(IV) which, while the charging is taking place, rects in part in Ni (II) resulting in a small amount of Ni(III) or is partially decomposed in Ni(III). This interpretation conforms with the assumption of Forrester (Ref.30) and Glemser and Einerhand (Ref.26). Briggs and his associates (Ref. 25) have already found, in the charged electrode, nickel in its 3 valence states, but consider that oxidation ocuurs in two distinct

stages; first the oxidation of Ni (II) into Ni (III) and later the Ni(III) → Ni(IV) and that the discharge is a process inverse to the charge. If we admit that the Briggs interpretation, the magnetic variation during the charge and the discharge should be following the sections AB and BC (Fig.21). However, our results show that this hypothesis should be rejected inasmuch as, from the start of oxidation, the points diverge from AB, which would prove the formation of Ni(IV).

The interpretation of the discharge curve (Fig.22) which is presented under the form of a sharp decrease in the potential, followed by 2 successive levels of approximately 0.4V and 0.0V has been the subject of numerous controversies (Ref.1). We may examine the validity or inconsistency of the various hypotheses voiced compared with the magnetic results obtained.

First of all, the initially sharp drop of the potential to approximately 0.4V has been attributed to the reduction of Ni(IV) in Ni(III). In this case, on one side, the relation O_{act}/Ni of the electrode whose potential is situated at the start of the first level shoud be exactly equal to 0.5. In reality, however, the first level is reached after about 30 min. of discharge and the O_{act}/Ni relation is, by this time, superior to 0.6 (Table IX). On the other side, the magnetic susceptibilities should then be located on the BC section. Yet, it is not what we observe in Fig. 21. Another hypothesis consists in admitting the reduction of absorbed oxygen in NiOOHβ. The determination of the oxidation

degree and of the magnetic susceptibility which regularly and continuously increases during the discharge process proves that the hypothesis is not correct.

Finally, during the second level of discharge it is generally admitted that NiOOHβ is reduced into $Ni(OH)_2$ or $Ni(OH)_4$. In reality, Fig.21 shows that Ni(IV) and Ni(III) are reduced simultaneously into Ni(II) and the satisfying alignment of the experimental points indicates that the relation Ni(III)/Ni(IV) is constant during the entire discharge and is superior to the relation Ni(III)/Ni(IV) as determined by the alignment of experimental points relating to the charge. This deviation between the relative proportions of Ni(III) and Ni(IV) during charge and discharge already evidenced by Briggs (25) by means of measuring the potential, may be explained by an initial reduction of Ni(IV) in Ni(III) until the relation Ni(III)/Ni(IV) achieves a certain value, approximately equal to 1 as it appears in Fig.21. This seems to show the relative stability of an intermediary oxide of the Ni_3O_5 formula (or rather Ni_2O_4H) which would contain an equiatomic mixture of Ni(III) and Ni(IV). The fact that we could not prepare, by chemical processes, hydroxides with a relation O_{act}/Ni superior to 0.75 (Table III) is equally in favor of the existence of such an intermediary oxide.

Finally, the second level of discharge whose existence is not obligatorily connected with the presence of graphite in the electrode has been attributed to either the reduction of oxygen absorbed by $Ni(OH)_2$ or to the reduction of the intermediary ox-

ide $Ni_3O_2(OH)_4$. The first hypothesis cannot be accepted, as the magnetic susceptibility should decrease at the end of the discharge. Yet Fig. 21 shows none of this. The second hypothesis could, on the contrary, be correct from the point of view of magnetism, yet the fact that the start and the end of this level cannot be directly attributed to a degree of oxidation well-established (*) and that its length is very variable, does not allow us to conclude on the $Ni_3O_2(OH)_4$ formation, rather than on some other intermediary oxide. In addition we should notice that if the polarization current is cut off, the potential initially located on this level immediately increases and attains a value corresponding to the first discharge level. If we admit the formation of an intermediary oxide, we may then think that the latter is superficially formed around a granule of active material, with the intermal part in a superior state of oxidation being protected and isolated from the electrolytical process. When we cut off the current, the ionic conductivity acting to the very interior of the granule gives to the electrode the highest potential corresponding to the first level. It is by an interpretation along the same lines that we find, in addition, in the works of Briggs (Ref.25)

(*) In Table IX we establish that an impregnated and polarized electrode under certain conditions, the start of the secod level appears at a relation of $O_{act}/Ni = 0.168$, while in another electrode subjected to an identical treatment the end of the second level appears at $O_{act}/Ni = 0.252$.

as well, that it is possible to explain why the electrode completely discharged is still oxidizing ($O_{act}/Ni = 0.06$). A superficial layer of $Ni(OH)_2$, non-conductive, covers the granule, leaving a certain amount of superior hydroxide protected from the electrolytic reduction; it depends on the size of the granule.

In conclusion we may give the following picture of the process of electrolytic polarization of $Ni(OH)_2$ in an alkaline medium. During the charge process the electrochemical oxidation, wjich is a very strong oxidation, causes in the crystalline lattice of $Ni(OH)_2$ the replacement of OH^- ions by O^{--} ions. This oxidation produces a decrease in the reticular volume of $Ni(OH)_2$, the ions Ni(III) and Ni(IV) being smaller then the Ni(II) ions, without an appreciable change in the structure.

The X-ray diffractograms obtained in the cases of the most oxidized compounds correspond to those of NiOOHβ. The compound Ni_2O_4H corresponds simply to the replacement of a half of the OH^- ions in NiOOH by the O^{--} ions and this is produced within one and the same phase. On the contrary, the diffraction beams broaden and become increasingly weaker, showing in this manner a strong distortion in the lattice.

During the discharge, in other words, during the electrochemical reduction, the OH^{--} ions substitute themselves for the O^{--} ions in an orderly manner, in such a fashion that the lattice at all times contains the same proportion of Ni(IV)/Ni(III) ions.

CONCLUSIONS

Chemical oxidation of nickel hydroxides by persulfate, hypochlorite and hypobromite of sodium produces superior nickel hydroxides in which the metal is engaged at the 3 and 4 valences.

The crystallographic study has revealed that the passage of $Ni(OH)_2$ into $NiOOH\beta$ is effected within the same phase.

The magnetic study has shown that all oxidizers do not affect $Ni(OH)_2$ in an identical manner. The persulfate of sodium, in fact, causes a very progressive oxidation with the nickel passing successively to the value 3 and 4, while the hypochlorite and hypobromite of sodium oxidize simultaneously Ni(II) into Ni(III) and Ni(IV) whose relative proportions may be calculated starting with the measuring of magnetic susceptibility and the degree of oxidation. Although these hydroxides do not completely obey the Curie-Weiss law, the thermomagnetic study has demonstrated that Ni(III) and Ni(IV) possess, respectively, 1 and 0 unpaired electrons.

The thermic decomposition of $Ni(OH_3)_2$, $6H_2O$ leads to NiO passing successively by the intermediary phases $Ni(NO_3)_2$, $4H_2O$, $Ni(NO_3)_2$, $2H_2O$ and $Ni(NO_3)_2$ in a vacuum and $Ni(NO_3)_2$, $4H_2O$, $Ni(NO_3)_2$, $2H_2O$, and $Ni(NO_3)_2$, $2Ni(OH)_2$ in open air and does not make possible the preparation of superior oxides of nickel. The magnetic constants of these nitrates of nickel have been established.

The action of sodium peroxide on the nickel and hydrolysis give us $NiOOH\gamma$ which, as $NiOOH\beta$ possesses one unpaired electron.

Finally, we have achieved a magnetochemical investigation of the evolution of nickel hydroxides during polarization either in the presence of graphite mixed with $Ni(OH)_2$, or in using a sintered platinum electrode impregnated with $Ni(OH)_2$. We have examined the validity of various hypotheses voiced on the process of electrolytic polarization depending on results obtained and given an interpretation compatible with the results of the considered phenomenon.

We have also established a deep analogy between the chemical oxidation (except in the case of persulfate) and the electrochemical oxidation of $Ni(OH)_2$ which is manifested from the very beginning by the appearance of ions of Ni(IV) as evidenced in Figs 2 and 21 by the position of the experimental data inside the ABC triangle, while during a progressive oxidation of Ni(II) into Ni(III) and Ni(IV) (case of persulfate) the points are aligned along the Ab and BC.

We emphasize, in addition, the efficiency of the magnetic investigation which allowed us to show the existence of the tetravalence of nickel there, where other investigative means, such as chemical or crystallographic analyses have been proven to be failures.

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